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## ASSAYER'S GUIDE

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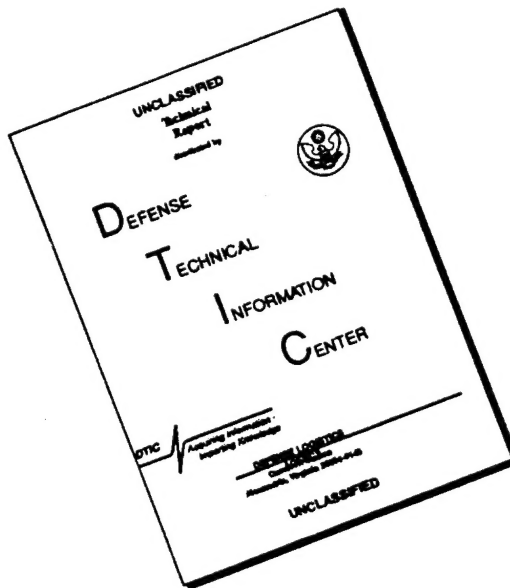
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## ASSAYER'S GUIDE

### INTRODUCTION

The determination of uranium and thorium in ores and rocks of domestic origin has become of increasing importance, owing to the recent developments in atomic energy. The procedures given in this circular deal primarily with methods of analysis for pitchblende, carnotite bearing sandstone, shales, phosphate rock and monazite sands. With but minor variations they are applicable to other types of material.

The quickest way to determine uranium or thorium is by making use of the natural radioactivity of these elements, but, unfortunately, there are several drawbacks. It is necessary that only uranium or thorium be present in the ore and that the element in question is in equilibrium with its radioactive dissociation by-products. While in some ores and minerals equilibrium has been reached, in other cases such as the carnotite bearing sandstone of the Colorado Plateau radioactive methods are not reliable. Generally, expensive equipment and trained personnel are necessary to obtain reliable results. For these reasons, methods depending on natural radioactivity are not discussed in this circular.

Chemical methods are more accurate and are to be preferred for contractual assays.

The following methods represent acceptable methods which have been used in the analysis of the materials mentioned above. A more detailed discussion of chemical methods of analysis may be found in the literature. As is usual in analytical chemistry, it is advisable to

use analyzed samples for testing of procedures. Analyzed samples of various types of material can be procured from Raw Material *Operations* ~~Section, New York Operations Office~~, United States Atomic Energy Commission, P. O. Box 30, Ansonia Station, New York 23, New York.

DETERMINATION OF  $U_3O_8$  IN PITCHBLENDReagents:

Potassium dichromate solution - 0.0270 N. Dissolve 1.3238 g of purified potassium dichromate in water and dilute to exactly 1 liter.<sup>1</sup>

Phosphoric - sulfuric acid mixture - Mix 350 ml phosphoric acid (85%) with 150 ml concentrated sulfuric acid.

Indicator solution - Add 0.32 g of barium diphenylaminesulfonate to 90 ml water. Stir and add 0.5 g of anhydrous sodium sulfate. Mix thoroughly, and allow to stand overnight. Filter through a #42 Whatman filter paper, and dilute the filtrate to 100 ml.

Ferric chloride solution - Dissolve 4 g  $FeCl_3 \cdot 6H_2O$  in 100 ml water.

Cupferron solution - Dissolve 6 g cupferron in 100 ml water.

Procedure:

## A. Solution of the sample

Weigh 2.000 g of the finely ground ore and transfer it to a 250 ml beaker. Wet the sample with water and add 30 ml nitric acid (1 + 1). Cover the beaker and heat on a hot plate at low heat for 2 hours. Add 12 ml sulfuric acid (1 + 1), continue heating on low heat for another hour. Then tip the watch glass and increase the heat of the hot plate to high heat. Continue the heating until the sulfur trioxide fumes are evolved, and then fume for 3 minutes. Cool, add 90 ml water, and heat on the hot plate to dissolve the soluble material.

### B. Hydrogen Sulfide Precipitation

Transfer the solution of the ore to a 500 ml suction flask, rinse out the beaker thoroughly with a stream of water from a wash bottle. Place a stopper loosely in the neck of the flask and pass a stream of hydrogen sulfide into the flask through the side arm. Continue the gasping for about 30 minutes, then cork up the side arm and tighten the stopper in the neck of the flask and allow to stand overnight. Then filter through a #40 Whatman filter, and wash the precipitated sulfides thoroughly with sulfuric acid (2 + 98) that has been saturated with hydrogen sulfide. The filtrate and washings should have a volume of about 225 ml when the washing has been completed. Evaporate the filtrate to 90 ml on the steam bath or hot plate.

### C. Cupferron Separation

Add 10 ml sulfuric acid (1 + 1) to the evaporated filtrate, heat to boiling, and add 2% potassium permanganate until the solution is pink. Cool in an ice bath until the temperature of the solution is at least 5° C. Transfer the solution to a 300 ml separatory funnel, add 25 ml of 6% cupferron solution in water, shake and allow to stand for a few minutes. Add 25 ml chloroform and shake vigorously. Allow to stand until the aqueous layer and the chloroform layers have completely separated. Drain off almost all of the chloroform layer into a beaker and repeat the extraction with chloroform until the chloroform layer is colorless. Add 5 ml of 6% cupferron solution, and if the precipitate is white and remains white after standing for a short time and does not impart a brown color in the next chloroform extraction, the extraction is finished. If not, continue the extraction

until the precipitate, formed by the addition of more cupferron, is white. The greenish tinge which is present in the chloroform layer when the extraction is complete is due to excess cupferron which is extracted by the chloroform.

Transfer the aqueous layer back into the original 250 ml beaker, add 15 ml concentrated nitric acid, cover with a speedy-vap watch glass and evaporate to sulfur trioxide fumes on a hot plate. Increase the heat and fume strongly for 3 minutes. Cool, wash down the sides of the beaker and watch glass with at least 15 ml of water, and add 1 ml perchloric acid. Evaporate, fume again, cool and wash down the sides of the beaker and watch glass, and then fume again. Four fumings are necessary to remove the cupferron decomposition products and nitric acid from the solution. After the last fuming, cool, add about 50 ml of water and heat to get all salts in solution. Sometimes most of the sulfuric acid is removed by the repeated fumings and so more must be added. The acid concentration of this last solution should be 5%, the volume from 50 to 75 ml, and more acid should be added if necessary.

#### D. Reduction of the Solution

Heat the solution to boiling and add a 2% potassium permanganate solution drop by drop, until the solution is pink. Cool in an icebath to room temperature and pass the solution through a clean Jones reductor<sup>2</sup> followed by three 30 ml portions of 5% sulfuric acid and then by three 30 ml portions of water. The rate of flow through the reductor should not be too fast, about 75 ml per minute. Three to four minutes should be allowed for the reduction if a reductor with a large amount of zinc is used.<sup>3</sup>



.. Titration of the solution

Transfer the reduced solution to a 600 ml beaker and aerate by bubbling air through the solution for 15 minutes. Wash off the watch glass cover and the aerator carefully. Then add 20 ml of freshly prepared 4% ferric chloride solution, stir, add 15 ml of the phosphoric-sulfuric acid mixture and 8 drops of diphenylaminesulfonate indicator. Titrate with 0.0270 N potassium dichromate solution until a permanent purple color is obtained. One ml/0.0270 N potassium dichromate is equivalent to .003791 g  $U_3O_8$ .

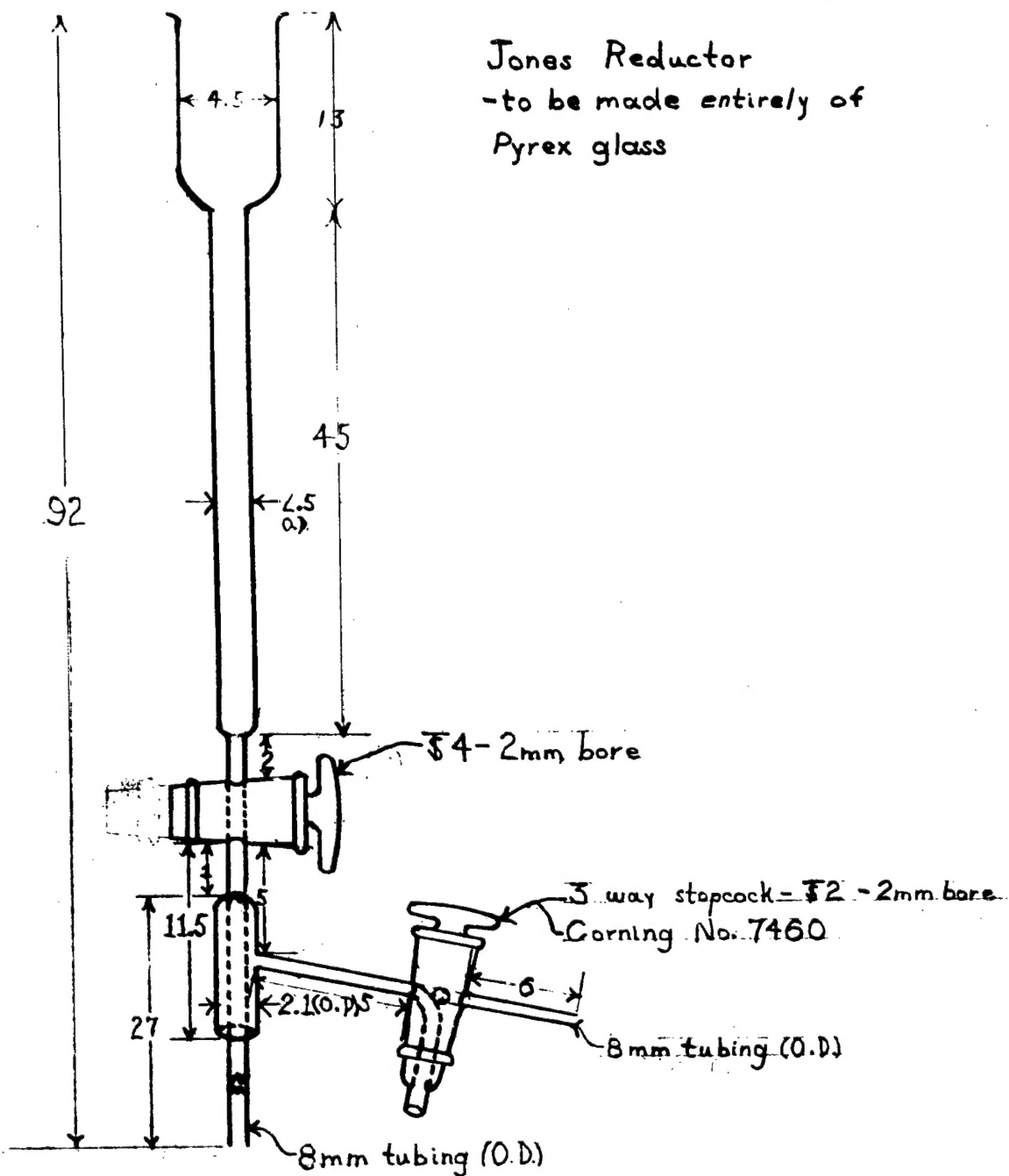
NOTES

<sup>1</sup> Unless the potassium dichromate is known to be pure, it should be purified as follows:<sup>1</sup> Recrystallize the purest grade of the salt at least three times and dry the crystals, finally at 150° C. Grind to a fine powder, and again dry at 150° C to constant weight. Keep the prepared salt in a glass ground-stoppered bottle. If the exact strength of a prepared solution is desired it is usually better to carefully weigh the purified salt, dissolve in water, and dilute to an exact volume or weight, than to rely on standardization by titration. If, as is usually the case, the performance of the solution is in question, it had better be standardized against like material which has been carefully standardized and which is carried through the method that is to be used. Dichromate solutions are very stable.

<sup>2</sup> A sketch of the Jones reductor in use at the National Bureau of Standards is attached.

<sup>1</sup> Hillebrand and Landell, Applies Inorganic Analysis, page 147 (1929)

Jones Reductor  
-to be made entirely of  
Pyrex glass



all measurements in centimeters unless  
otherwise specified.

### 3 Preparation of the Jones reductor:

To prepare the amalgamated zinc for the reductor: Dissolve twenty-six grams of mercuric chloride in 750 ml of hot water containing five ml of nitric acid. When all the mercuric chloride is in solution, cool the flask and contents to room temperature, add 700 g of zinc metal (20 mesh) and shake the flask and contents thoroughly for two minutes. Wash the amalgamated zinc in the flask several times with water and several times with sulfuric acid (5 + 95) before transferring to the reductor. Wash the reductor each time before it is used with at least 100 ml of sulfuric acid (5 + 95) and 100 ml of water. Keep the reductor full of water when it is not in use.

DETERMINATION OF  $U_3O_8$  IN LOW GRADE ORES AND SANDSProcedure

The sample should be 100 mesh or finer. Transfer an appropriate weight (10 g is adequate for material of 0.3%  $U_3O_8$  content) to a 400 ml beaker and add 10 to 20 ml of nitric acid, 20 to 30 ml of sulfuric acid (1 + 1), 2 to 3 ml of perchloric acid (70%) and 5 ml of hydrofluoric acid; stir well and heat on a steam bath temperature for 5 to 10 minutes to allow the  $H_2SiF_6$  and excess hydrofluoric acid to be largely expelled; then cover and evaporate to dense fumes of sulfur trioxide. Allow to cool, and rinse off the cover glass and the sides of the beaker. Dilute till the acidity is 10 per cent, stir well, and digest to obtain complete solution of all soluble salts.

Cool to approximately 10° C, add an excess of 2.5 per cent potassium permanganate solution (3 to 5 drops is usually enough) and some ashless paper pulp, then add a freshly prepared six per cent aqueous solution of cupferron, dropwise, with vigorous stirring, until a snow-white precipitate that quickly dissolves is noted, indicating complete precipitation. Continue the vigorous stirring for several minutes longer. Filter on a Whatman #40 or equivalent paper, using paper pulp, and wash four to five times with cold sulfuric acid (5%) containing 5 ml of the cupferron reagent per liter. Collect the cupferron filtrate and washings in a 500 ml narrow mouth Erlenmeyer flask, add a few glass beads, and boil down to a volume of approximately 150 ml. Remove from the heat, cautiously add 30 ml of nitric acid and

2 ml of perchloric acid (70%), and evaporate to very dense fumes of sulfur trioxide to destroy all organic matter and expel excess perchloric acid. Allow to cool, rinse down the sides of the flask with about 25 ml of water, boil for several minutes; then add an excess (2 to 3 drops) of potassium permanganate solution (2.5%) and repeat the evaporation to dense fumes of sulfur trioxide.

Allow to cool, add 100 ml of hot water, heat until all salts are in solution, dilute to a volume such that the acid strength will be about six per cent, and cool to 20° C. Pass the cooled solution through the amalgamated zinc reductor at a rate of about 10 ml per minute, and follow with at least three washes of 50 ml of cold water. Aerate the reduced solution by passing air at 3 to 5 psi. through a tube into the solution for 10 to 15 minutes and then titrate to a clear blue end point with 0.02 N potassium permanganate solution using exactly two drops of a 0.025 molar o-phenanthroline-ferrous complex solution as indicator. 1 ml of .02 N potassium permanganate equals .002505 g  $U_3O_8$ .

The procedure for preparing the standard potassium permanganate solution is as follows:<sup>(1)</sup>

Dissolve about 3.2 g. of C. P. potassium permanganate in 1 liter of water, heat the solution to boiling, and keep slightly below the boiling point for an hour. Alternatively, allow the solution to stand at room temperature for two or three days. Filter the liquid through pure asbestos (free from organic matter) or through a sintered-glass filter crucible. Transfer the filtrate to a clean

(1) Kolthoff, I. M. and Sandell, E. B. Textbook of Inorganic Analysis, p. 592, (1946). The MacMillan Co., New York.

Glass-stoppered bottle freed from grease with cleaning mixture. Protect the solution from evaporation, dust, and reducing vapors, and keep it in the dark or diffuse light. If in time manganese dioxide settles out, refilter the solution and restandardize it.

If 0.02 N permanganate is required, it is prepared by dilution of 0.1 N solution with a good grade of water. The dilute solution should be prepared just before use and should not be stored for any length of time, because of the relatively rapid rate of deterioration.

For the standardization of the above 0.1 N solution, the following procedure is described in the provision certificate of Analysis of Standard Sample 40e Sodium Oxalate.

Drying - Sample No. 40e is not appreciably hygroscopic.

However, for an accuracy of better than 1 part in 1000 the sample should be dried for 1 hour at 105° C.

Standardization of 0.1 N permanganate. - Transfer 0.3 g of sodium oxalate (dried at 105° C) to a 600 ml beaker. Add 250 ml of diluted sulfuric acid (5 + 95) previously boiled for 10 to 15 minutes and then cooled at 27° C  $\pm$  3°. Stir until the oxalate has dissolved. Add 39 to 40 ml of 0.1 N potassium permanganate at a rate of 25 to 35 ml per minute while stirring slowly. Let stand until the pink color disappears (about 45 seconds). Heat to 55° to 60° C and complete the titration by adding permanganate until a faint pink color persists for 30 seconds. Add the last 0.5 to 1 ml dropwise, with particular care to allow the solution to become decolorized before the next drop is introduced.

Determine the excess of permanganate required to impart the

permanent pink color to the solution. This can be done by matching the color by adding permanganate to the same volume of the specially treated dilute sulfuric acid at 55° to 60° C. This correction usually amounts to 0.03 to 0.05 ml.

### NOTES

#### Cupferron Precipitation

The precipitation by cupferron is extremely important in this method. Although the occlusion of uranium by the metal cupferrates is negligible with moderate amounts, the retention rises very abruptly with excess of the cupferron reagent, resulting in as much as 5% of the uranium being held up with 50 ml excess of the 6% reagent. The solution should be ice cold, with not less than 7.5% nor more than 10% sulfuric acid by volume. The precipitation should be made very slowly with vigorous stirring, allowing time to react and flocculate. With practice and care, excess of the reagent can be avoided. The metal cupferrates are slightly soluble even in the wash solution so that too thorough washing of the precipitate is not desirable. When the precipitate is bulky and requires considerable washing, it is best to boil down the filtrate, destroying the reagent, and again to precipitate with a small amount of cupferron to remove the last traces of iron or vanadium.

#### Fuming Filtrate after Cupferron Precipitation

Nitric and perchloric acids, as well as the excess cupferron, must be removed from the filtrate. Complete fuming is usually indicated by the salting out of a double basic sulfate of aluminum and manganese

which is blue in color.

#### Reduction

The reductor must be cleaned and renewed frequently. Of the elements that pass through the cupferron precipitation and are held up in the reductor, the most commonly encountered are arsenic, copper and selenium. These do not interfere with results providing they are held up in the reductor. However, with continued use of the reductor, they will gradually work down through with some mercury as the zinc loses its amalgamation, thereby causing high results with fading end points.

#### Blank

The titration indicator solution must be dispensed with the dropper or burette always in the same position, in order to give drops as nearly equal in volume as possible for all determinations. The blank used should be that of the complete method and not only of the reductor and indicator solution.



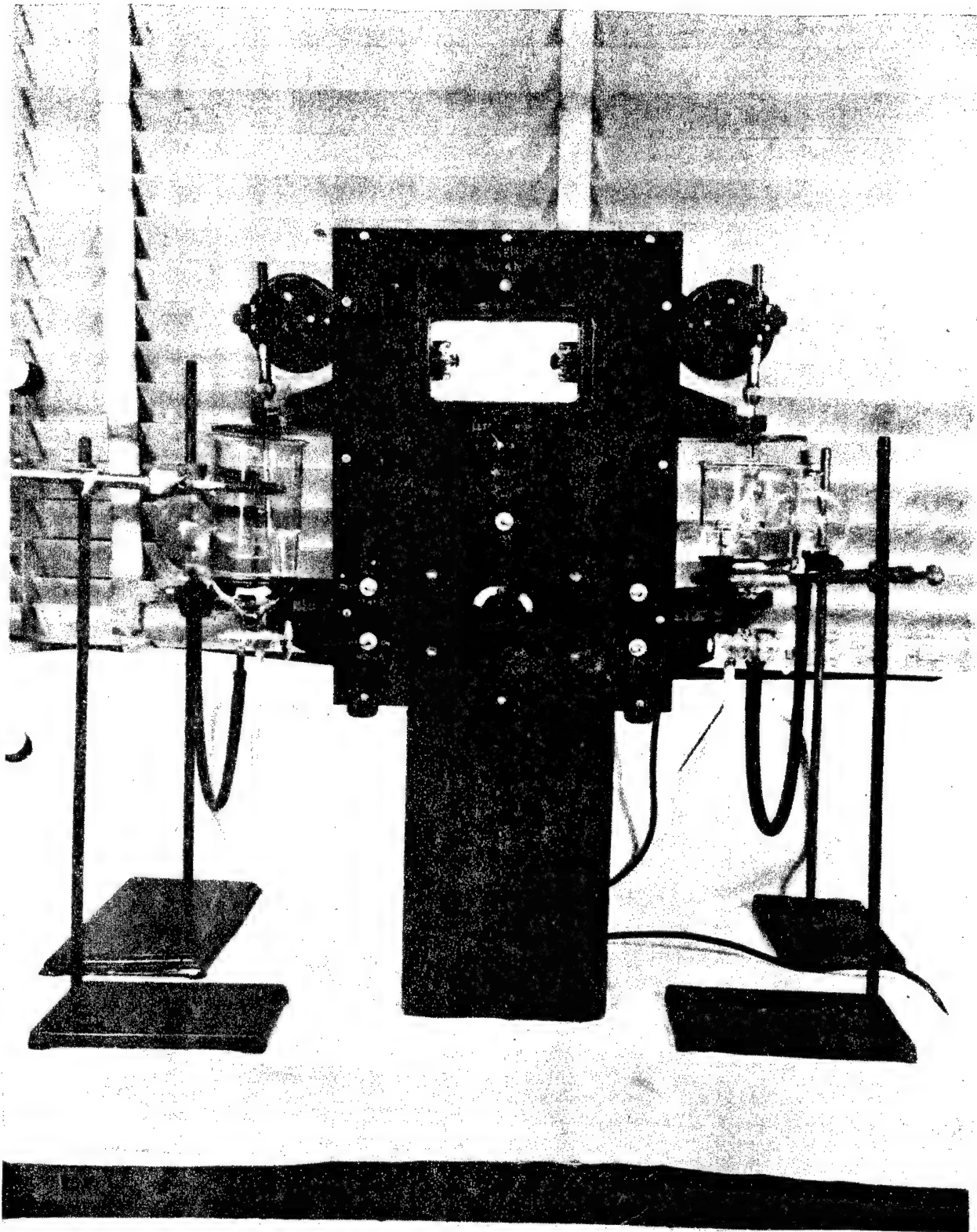
**DETERMINATION OF  $U_3O_8$  IN ORES HIGH IN ARSENIC AND HEAVY METAL.**

Weigh a 2.0000 sample of the ore into a 500 ml Erlenmeyer flask, add 20 ml of hydrochloric acid (1:1) and 10 ml nitric acid (1:1). Boil the mixture for a short time and then add 16 ml of sulfuric acid (1:1). Heat on the hot plate until fumes of sulfur trioxide are evolved. Cool, wash down the side of the flask with water, and add 20 ml of hydrobromic acid (1:1) and 15 ml of hydrochloric acid (1:1) and heat the solution again until sulfur trioxide fumes are evolved. Cool, and repeat the treatment with hydrochloric acid and hydrobromic acid to complete the removal of the arsenic. Cool the flask, wash down the side of the flask with water, add 10 ml of nitric acid, and heat again until sulfur trioxide fumes are evolved. Fume the solution three times and wash down the sides of the flask each time after each fuming.

After the last fuming, add 90 ml of water, and heat the solution to boiling to dissolve all soluble salt. Filter the solution through a #1 Whatman filter paper and wash the residue through with hot water. Discard the residue. Evaporate the filtrate to a volume of 100 ml and cool to room temperature.

An apparatus as shown in the illustration is used for the mercury cathode purification.

Pour sufficient mercury through the leveling bulb into a Melvern electrolytic cell to bring the mercury level of the cell to a point of maximum surface area. Transfer the filtrate to the cell and wash out the flask with 100 ml of water and add this to the cell. Connect the



platinum anode to the position wire, and insert the cathode into the mercury column of the levelling bulb. Insert the glass stirrer so that the blade just breaks the surface of the mercury and cover the cell with a split watch glass. Electrolyze the solution for 1 hour at a current of approximately 5 amperes, and for one hour at a current of 2 amperes with continuous stirring. When the electrolyzing is complete, stop the stirrer, and drain the mercury from the cell, leaving a portion of the mercury in the stopcock bore. Drain the sample into a 800 ml beaker, close the stopcock, and wash down the cover glass and cell wall with 20 ml of sulfuric acid (1† 49). Return the mercury to the cell and electrolyze the solution for 5 minutes. Drain the wash solution from the cell into the 800 ml beaker containing the first solution.

Evaporate the electrolyzed solution to a low volume on the steam bath. Add 5 ml of nitric acid, and heat the solution until sulfur trioxide fumes are evolved. Cool, add 100 ml of water, heat to dissolve the sample, and transfer the resulting solution to a 500 ml Erlenmeyer flask. Evaporate the solution to a volume of 90 ml, add a solution of potassium permanganate until the solution is pink, then cool the flask and contents in an ice bath to a temperature below 5°C.

Transfer the solution quantitatively to a 300 ml separatory funnel, add 25 ml of 6% cupferron and shake for one minute. Add 25 ml of chloroform and shake the funnel and contents again for 1 minute. Allow the layers to separate, draw off the chloroform layer into a beaker leaving a little chloroform in the funnel to prevent any loss

of uranium with the aqueous layer. Repeat the extraction with chloroform until the chloroform layer is pale green or colorless. Then add another 5 ml of the cupferron solution and shake. If the precipitate is white and does not impart a brown color to the chloroform layer in the subsequent extraction, the separation of the cupferride is complete; otherwise, further extraction with chloroform is necessary. A greenish tinge in the chloroform layer, even upon complete extraction, is due to excess cupferron being extracted by the chloroform.

Transfer the aqueous layer from the separatory funnel to the original 500 ml Erlenmeyer flask, and wash the funnel twice with portion of water. Add 15 ml nitric acid, and a few glass beads and heat the solution until fumes of sulfur trioxide are evolved, and sulfuric acid refluxes up the sides of the flask. Cool, wash down the sides of the flask with water, add 1 ml of perchloric acid, and heat again as before. Four fumings are necessary to remove excess nitric acid and the organic decomposition products of the cupferron.

Following the final fuming, cool the sample, add 50 ml of water and heat to dissolve the sample. Add 2% potassium permanganate to the hot solution until permanently pink. Cool the solution in an ice bath to room temperature, and pour through a clean Jones Reductor at the rate of 30 to 40 ml per minute. Following the sample, pour through the reductor thirty ml portion of sulfuric acid(1+19) and finally three thirty ml portion of water, as a wash solution.

Transfer the reduced solution to a 600 ml beaker and aerate for 15 minutes. At the end of this time wash the cover glass, aerator and the side of the beaker with water. Add 20 ml of a freshly prepared solution of 4% ferric chloride, stir, then add 15 ml of sulfuric-phosphoric acid mixture, and finally 8 drops of dephanylamine indicator. Titrate with the standard 0.0270 N potassium dichromate, to a permanent purple color.

The standard potassium dichromate is prepared as described in the method for determining  $U_3O_8$  in pitchblende.

DETERMINATION OF URANIUM IN ORES  
HIGH IN ARSENIC AND HEAVY METALS

MODIFIED PROCEDURE<sup>1</sup>

Weigh a sample between 0.5 g and 5.0 g, depending upon the uranium content, into a 400 ml beaker. Add 10 ml of nitric acid (1 + 1) and heat to boiling. Add 12 ml of sulfuric acid (1 + 1), and if the ore contains much silica, add a little hydrofluoric acid. Heat to fuming and fume for 5 minutes. Cool, add 30 ml of hydrobromic acid (48%), warm carefully until most of the bromine has been driven off, and again heat to fumes of sulfur trioxide. Cool, wash down the sides of the beaker and fume again to eliminate any traces of bromine. Cool, add 50 ml of water and let stand until the lead sulfate and silica settle. Filter the solution and wash the precipitate with cold sulfuric acid (1 + 99).

Add ammonium hydroxide (1 + 1) to the filtrate until it is just alkaline to methyl orange. Add 4.0 ml of sulfuric acid (1 + 1) and dilute the solution to 100 ml. Electrolyse the solution in a modified Melaven mercury cathode cell for 30 minutes at 7 amperes and 7 volts.<sup>2</sup> Test for the complete removal of Cu, Ni, Co, and Fe as follows: Place 1 drop of the acid test solution from the electrolyse cell, 1 drop of 1% zinc acetate and 1 drop of ammonium mercury thiocyanate (5 grams mercuric chloride + 9 grams ammonium thiocyanate + 100 ml water) in a depression on a white porcelain spot-plate. Mix with a stirring rod. If no color results then Cu, Ni, Co and Fe have been completely removed from the solution. The precipitate of zinc mercury thiocyanate is colored violet by copper, gray-green by nickel, blue by cobalt and reddish-brown by iron.

With the current still flowing, remove the solution from the cell and wash the mercury with 50 ml of sulfuric acid (1 + 99). Combine the solution and washing and, if necessary, filter them through a fine filter paper with the addition of more paper pulp. Wash the precipitate with sulfuric acid (1 + 99). Add 16 ml of sulfuric acid (1 + 1) and evaporate to 100 ml.

By this procedure the following elements, if present, are quantitatively removed: Fe, Co, Ni, Cu, Zn, Ga, Ge, Rh, Pd, Ag, Cd, In, Sn, Ir, Pt, Au, Hg, Tl, Cr, Mo, Re, Po, Bi, As, Se, Te, Pb, and Os. The elements partially removed are: Mn, Ru and Sb.<sup>3</sup>

Heat the solution nearly to boiling and add 3% potassium permanganate dropwise, until slightly pink. Cool to 5 degrees Centigrade or lower. Transfer the solution to a 600 ml, pear-shaped, separatory funnel and add 15 ml of cold 6% cupferron solution until a white precipitate appears which redissolves quickly. Extract the cupferrids with 15 to 20 ml portions of chloroform until the aqueous layer is water-white. Add another 5 ml of 6% cupferron. The precipitate formed should be white. If not, add additional cupferron solution. Extract again with chloroform until the chloroform layer is water-white. This procedure separates hexivalent U from Cb, Ta, W, Th, Co, Ti, V and Zr.

Transfer the aqueous layer to a 600 ml beaker, add 10 ml of concentrated nitric acid and warm gently until all the chloroform is expelled. Then heat until sulfur trioxide fumes are evolved. Cool, wash down the sides of the beaker and again heat to fumes of sulfur trioxide. Repeat the washing and fuming. Add 2 ml perchloric acid (60%) and again fume strongly. Wash down the sides of the beaker and fume again.

Nitrates should now be absent. Adjust to 2 ml sulfuric acid, cool and dilute to 50 ml. To ensure absence of nitrates, add a few drops of potassium permanganate (1 + 99) until the solution is pink.

Pass the sulfuric acid (4%) solution through a Jones Reductor at a moderate rate and wash the reductor first with 90 ml sulfuric acid (5 + 95) and then with 90 ml of distilled water, collecting the solution and the washings in a 600 ml beaker. Aerate the solution for 10 minutes by using an 8 inch length of one-quarter inch glass tubing drawn to a fine opening.

Wash the tube, watch-glass and the sides of the beaker with water. Add 25 ml of freshly prepared 5% ferric chloride, 15 ml phosphoric acid-sulfuric acid mixture (73 ml phosphoric acid + 27 ml sulfuric acid) and 8 drops of 0.01 M sodium diphenylaminesulphonate. Titrate with a standard potassium dichromate using .02 N for low grade and .05 N for high grade ores until one drop changes the color from green to deep violet. Run a blank and deduct this value from the titration found.

The dichromate solution is made by weighing up the theoretical amount of the volumetric standard grade and dissolving in cold water. 1 ml .05 potassium dichromate = .007018 gram  $U_3O_8$ .

It has been found that the blank increases as the volume of dichromate is increased. To allow for this a series of standard uranium sulphate solutions are titrated with potassium dichromate and the actual titration value is plotted against the number of milligrams of  $U_3O_8$  present. A straight line is obtained and is used for determining the  $U_3O_8$  content of unknown samples. Thus, no blank correction needs to be applied to the titration value.



- <sup>1</sup> F. T. Rabbitts, Topical Report #6, Bureau of Mines, Canada
- <sup>2</sup> Mercury Cathode Cell for Rapid Electrolysis, F. T. Rabbitts, ANALYTICAL CHEMISTRY, Vol. 20, P. 181.
- <sup>3</sup> Outlines of Methods of Chemical Analysis, Lundell & Hoffman, 94-95, 117-118, Wiley (1929).

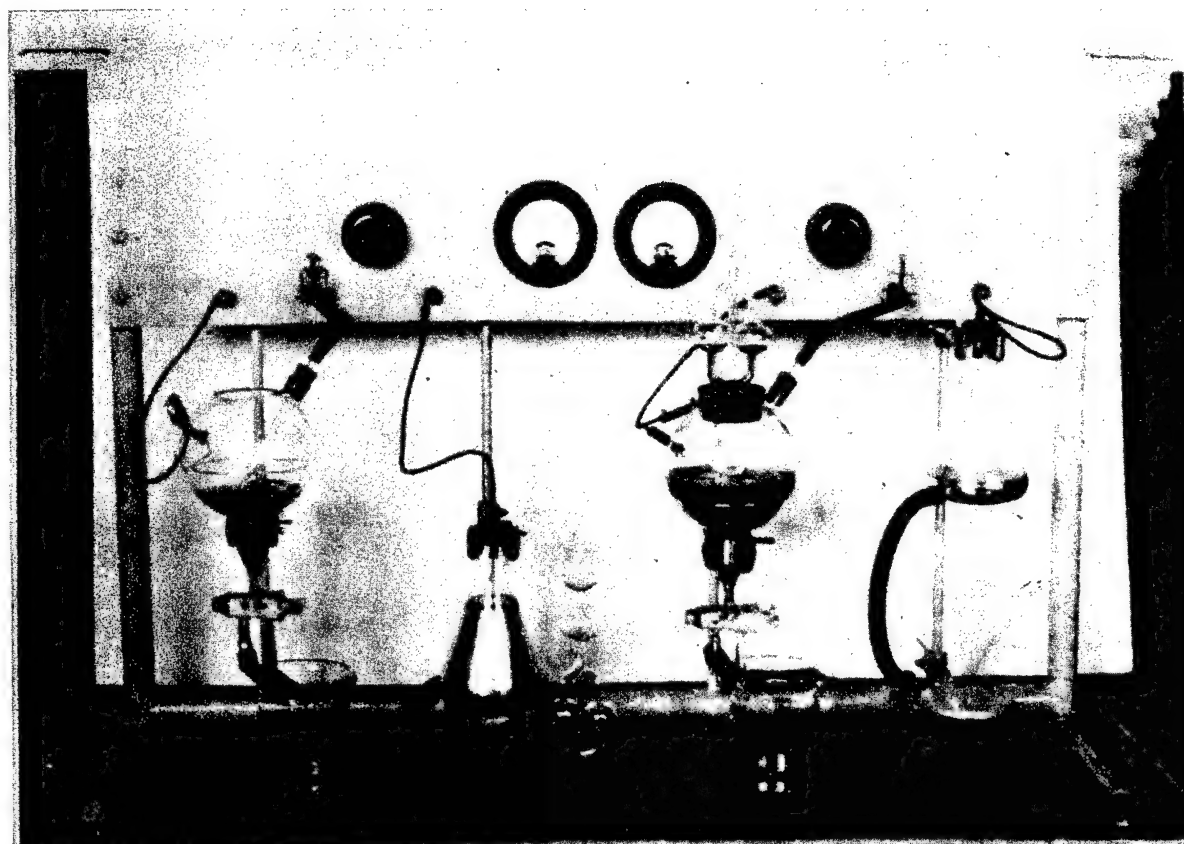
#### NOTES

##### Cleaning the Mercury

Use electrolytic method making mercury the anode; or use the method described in "Practical Physical Chemistry", A. Findlay, p. 197, Longman's, 7 Edit. (1941).

##### Application of Method

The method can be applied generally since it removes Cr, Ni, Co and other interfering elements which remain to cause difficulty after the usual hydrogen sulphide-cupferron separations. Phosphate, sulphate or other anions do not interfere.



Electrolytic Apparatus used at Bureau of Mines, Canada

COLORIMETRIC DETERMINATION OF  $U_3O_8$   
IN CARNOTITES AND LOW GRADE PITCHBLENDENES.

Weigh sufficient sample to contain between 5 and 20 mg of  $U_3O_8$ . Transfer to a 250 ml beaker. Add 25 ml of nitric acid (1+1), cover with a water glass and boil for about 5 minutes. Filter through a #40 Whatman filter paper. Rinse the beaker and wash the residue with hot water. Reserve the filtrate.

Place the filter paper and contents in a platinum crucible and burn off the filter paper. Cool, then moisten the residue with water and add 2 drops of sulfuric acid (1+1). Fill the crucible 3/4 full with hydrofluoric acid and heat to dryness on a hot plate.

Fuse the residue with 3-5 grams sodium carbonate. Swirl the crucible while the fusion is cooling. Dissolve the fusion in nitric acid (1+1) and combine with the filtrate from the original solution.

Heat the solution to boiling. Precipitate the  $R_2O_3$  group with ammonium hydroxide (1+1). After digestion on a steam bath, filter through a #42 Whatman filter paper. Test the filtrate for sulfate ion by acidifying with hydrochloric acid and adding barrium chloride solution. If sulfates are present, dissolve the  $R_2O_3$  precipitate with hot nitric acid back into the original beaker. Bring the solution to a boil and repeat the  $R_2O_3$  precipitation as many times as is necessary

to obtain a negative test for the sulfate ion in the filtrate.

Evaporate the final nitric acid solution to near dryness and dissolve any residue in 40 ml of nitric acid (1+4). Saturate the resulting solution with ammonium nitrate (about 60 grams are required).

Transfer the nitric acid solution of the sample saturated with ammonium nitrate to Part A of the continuous extractor. Take care that no sample is lost through the sidearm. A long stem funnel or stirring rod must be used. Some solid ammonium nitrate should be present.

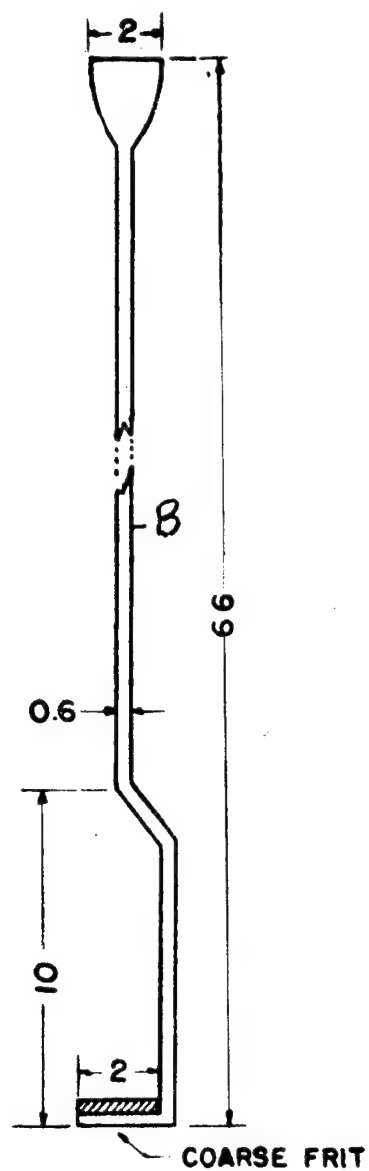
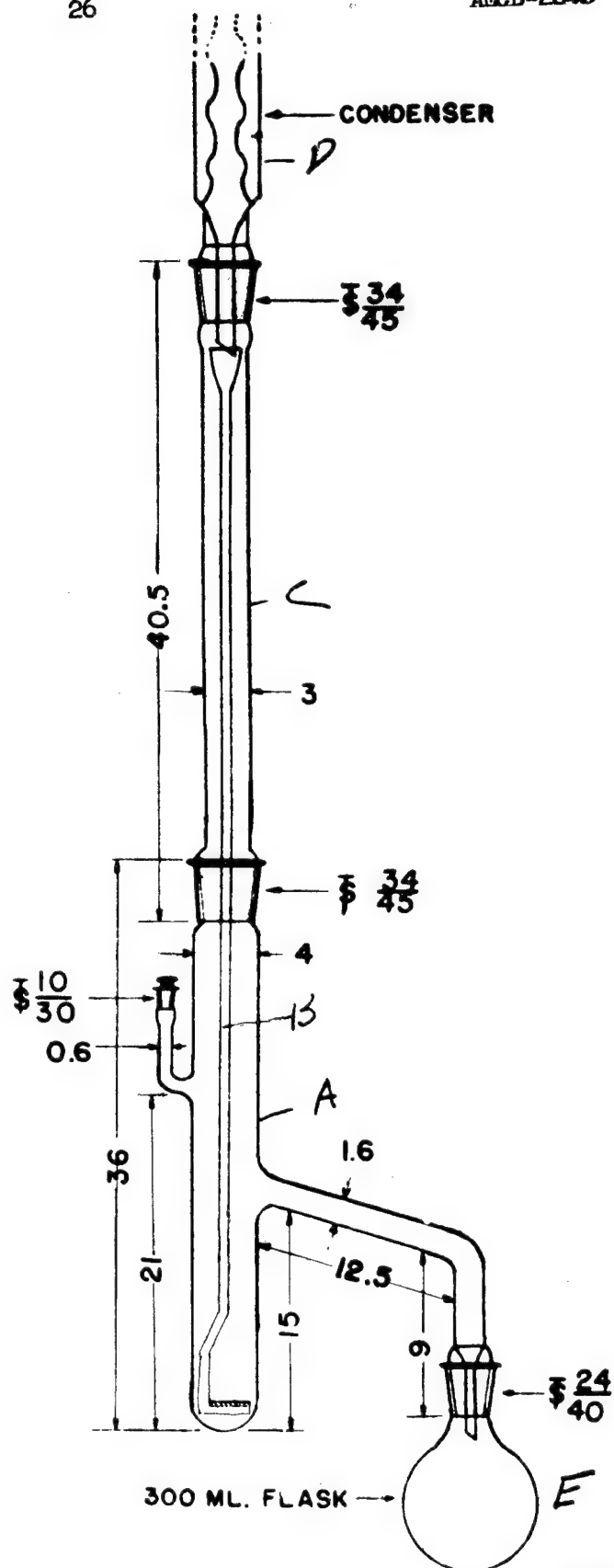
Pour ethyl ether into the thistle tube portion of the frit, part B of the extractor. The ether should tend to form a column. Place part B in position with the frit end at the bottom.

Use care in handling ether. Keep away from flames. No smoking in laboratory while extractors are being used.

Fill the receiving flask (E) 1/3 full with water and add enough ether to form a layer 1 inch thick. Attach the receiving flask (E) to the extractor (part A) as in the figure. Be sure the glass stopper is in place in the small sidearm on part A.

Attach the column C to part A as in the figure. This part may be warmed in hot water to hasten the start of the extraction.

Attach the condenser (part D) as in the figure and pass cold water through it continuously. If more than one extractor is being used, the condensers may be cooled in series (up through four extractors).



CONTINUOUS EXTRACTOR

DIMENSIONS IN CM.

Place a hot water bath on a round hot plate (set at "low") around the receiving flask E.

After a short time the ether from flask E will reflux from condenser D and drip into the thistle tube at the top of Part B. The ether will build up a column and begin to pass through the glass frit in tiny bubbles. The ether layer in part A will overflow into the receiving flask E. Operate as rapidly as possible without causing the ether in the receiving flask to boil.

After about 15 minutes, raise the column C and stir the water solution in part A by raising and lowering part B. Repeat every 15 minutes.

If any precipitates form, add 5 ml of concentrated nitric acid saturated with ammonium nitrate through the small sidearm opening in part A.

At the end of 90 minutes remove the water bath and allow the flask E to cool. Transfer the contents of the flask to a 400 ml beaker. Rinse the flask with most of the ether layer from extractor part A and add to the beaker. Wash the flask once with water, adding the wash to the beaker, and then place in the steam bath and evaporate to dryness.

Wash down the sides of the beaker with about 15 ml of nitric acid (1+1). Add 1 ml perchloric acid; 3 ml sulfuric acid and some glass beads. Cover beaker with a speedyvap watch glass and heat to fumes of sulfur trioxide. Allow the

sulfuric acid to reflux halfway up the sides of the beaker before removing from the hot plate. Cool.

Rinse the cover and sides of the beaker with not more than 75 ml of water. Neutralize with sodium hydroxide (1+1) then add 5 ml of sodium hydroxide (1+1) in excess. Dilute to a volume of 100 ml and add about 0.5 g sodium peroxide. Stir and filter through a double #40 Whatman filter paper into a 200 ml Erlenmeyer flask. Cover with a small watch glass and bring just to a boil to destroy the vanadium color. Cool to room temperature gradually.

Read the percent transmittancy with a Coleman or a Beckman spectrophotometer at a wave length of 425 mu. With a Beckman spectrophotometer, use 2 cm cells at the same wave length. Develop the color with known quantities of  $U_3O_8$  to obtain a transmittancy-concentration curve from which the amount of  $U_3O_8$  in the sample can be obtained.

COLORIMETRIC DETERMINATION OF  $U_3O_8$  IN SHALES

Weigh sufficient sample to contain between 200 and 600 micrograms of  $U_3O_8$  and transfer it to a small porcelain dish. Ignite the dish and content in a furnace, temperature not to exceed  $700^{\circ}C$  until all carbonaceous material is destroyed. Transfer the ignited sample to a platinum crucible, add 5 g of sodium carbonate and fuse for 30 minutes. Cool the crucible and contents, place in a beaker containing 50 ml of nitric acid (1 + 1). Warm the resulting solution and filter through a #42 Whatman filter paper. Wash the paper and residue through with hot water. Reserve the filtrate. Ignite the paper and residue in a platinum crucible until the filter paper is destroyed. Cool the crucible, moisten the residue with two to four drops of sulfuric acid (1 + 1). Place crucible on a hot plate, fill  $2/3$  full of hydrofluoric acid and evaporate to dryness.

Fuse the hydrofluoric acid residue with 5 g of sodium carbonate. Dissolve the cool melt in 40 ml of nitric acid (1 + 1) and combine with the filtrate from the original nitric acid treatment.

Heat the solution almost to boiling, and while still hot, precipitate the  $Fe_2O_3$  group with ammonium hydroxide (1 + 1). Allow the precipitate to settle and then filter the solution through a Whatman #42 filter paper. Test the filtrate for sulfate ion by transferring a portion to a test tube, acidifying with HCl and adding barium chloride (10%). If sulfate ion is present, as shown by the  $BaSO_4$  precipitate, dissolve the hydroxide from the paper with hot nitric acid (1 + 1), and repeat the ammonium hydroxide precipitate as many times as is necessary to obtain a negative test for the sulfate ion.



Dissolve the final ammonium hydroxide precipitate with hot nitric acid (1 + 1) and evaporate the solution almost to dryness on the steam bath and add 40 ml of nitric acid (1 + 5). To the solution add 5 g of ferric nitrate to complex the phosphates present, and enough ammonium nitrate to saturate the solution.

Transfer the nitric acid solution of the sample saturated with  $\text{NH}_4\text{NO}_3$  to Part A of the continuous extractor. Take care that no sample is lost through the side arm. A long stem funnel or stirring rod must be used. Some solid  $\text{NH}_4\text{NO}_3$  should be present.

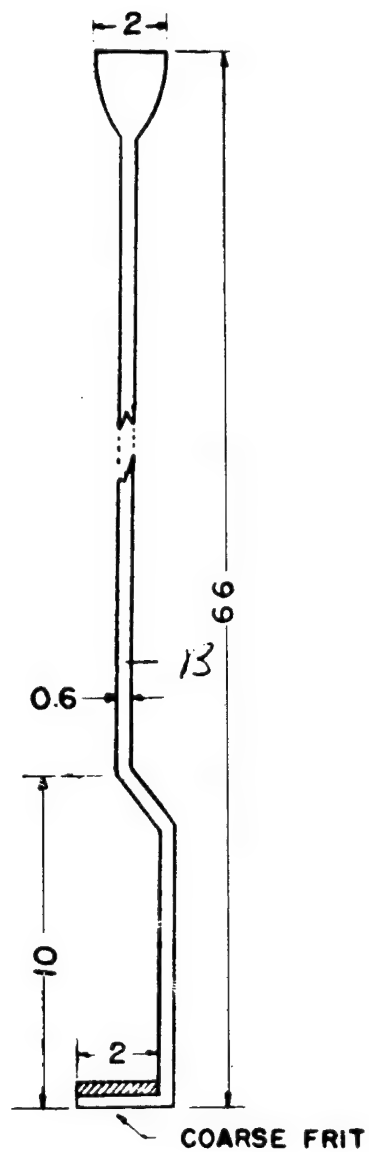
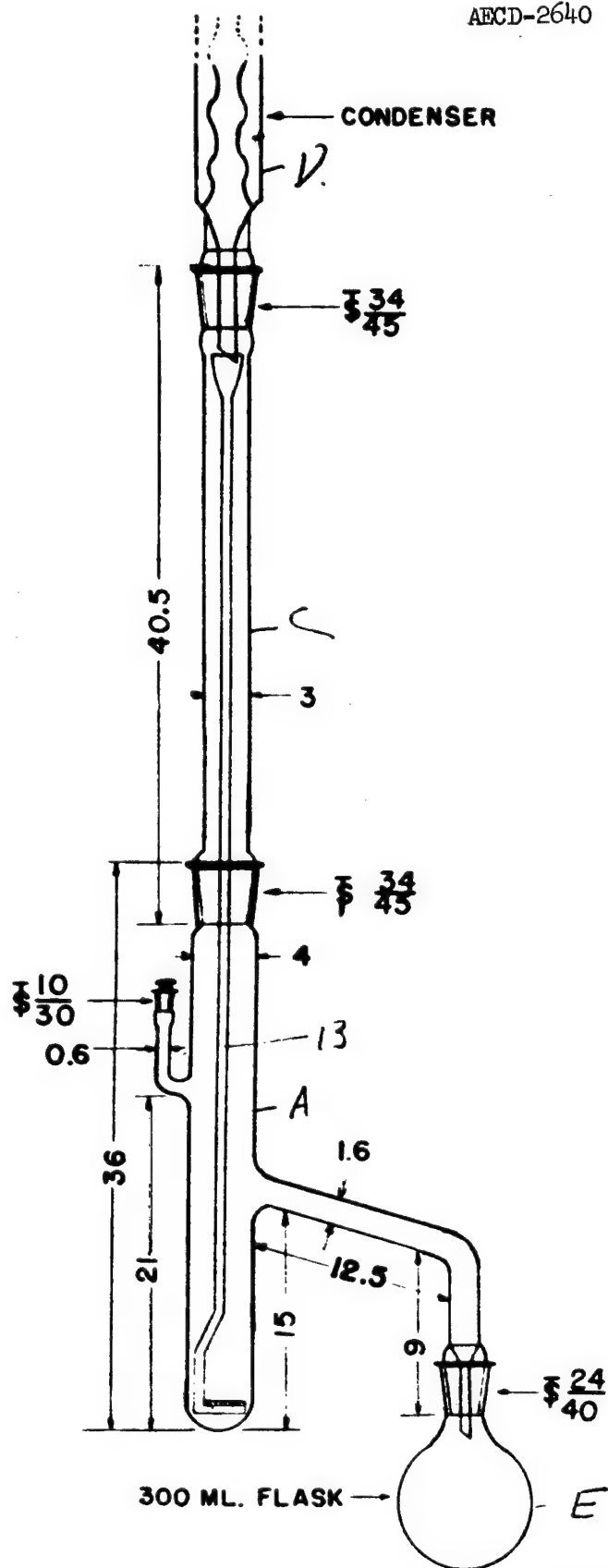
Pour ethyl ether into the thistle tube portion of the frit, Part B of the extractor. The ether should tend to form a column. Place Part B in position with the frit end at the bottom.

Fill the receiving flask (E)  $1/3$  full with water and add enough ether to form a layer one inch thick. Attach the receiving flask (E) to the extractor (Part A) as in the figure. Be sure the glass stopper is in place in the small side arm on Part A.

Attach the column C to Part A as in the figure. This part may be warmed in hot water to hasten the start of the extraction.

Attach the condenser (Part D) as in the figure and pass cold water through it continuously. If more than one extractor is being used, the condensers may be cooled in series (up through four extractors.)

Place a hot water bath on a round hot plate set at low heat around the receiving flask (E). After a short time the ether from flask (E) will reflux from condenser (D) and drip into the thistle tube at the top of Part B. The ether will build up a column and begin to pass through the glass frit in tiny bubbles. The ether layer in Part A will overflow into the receiving flask (E). Operate as rapidly as possible without causing the ether in the flask (E) to boil.



CONTINUOUS EXTRACTOR

DIMENSIONS IN CM.

After about 15 minutes, raise the column (C) and stir the water solution in Part A by raising and lowering Part B. Repeat every 15 minutes. If any precipitates form, add 5 ml of concentrated  $\text{HNO}_3$  saturated with  $\text{NH}_4\text{NO}_3$ , through the small side arm opening in Part A.

At the end of 90 minutes, remove the water bath and allow the flask (E) to cool. Transfer the contents of the flask (E) to a 400 ml beaker. Rinse the flask (E) with most of the ether layer from extractor Part A and add to the beaker. Wash the flask once with water, adding the wash to the beaker, and then place in the steam bath and evaporate to dryness.

Wash down the side of the beaker with 15 ml of nitric acid (1 + 9), add about 10 glass beads, 1 ml of perchloric acid (70%) and 2 ml of concentrated sulfuric acid. Cover with a speedyvap and heat until  $\text{SO}_3$  fumes are evolved. Continue the heating until the sulfuric acid refluxes halfway up the side of the beaker. Cool, rinse down the side of the beaker and wash glass with not more than 30 ml of water. Make the solution slightly alkaline with sodium hydroxide (1 + 1), and add 1 ml of 10% sodium peroxide solution. Transfer to a 50 ml volumetric flask. Add 2.5 ml of sodium hydroxide (1 + 1) and dilute to volume with water. Transfer the water solution back to the original beaker, and filter the solution through a dry #40 Whatman filter paper into a dry Erlenmeyer flask.

Read percent transmission with a Beckman spectrophotometer in 10 cm cells at a wave length of 390 mμ and a slit width of .03 mm. Read samples against  $\text{H}_2\text{O}$  and subtract amount of  $\text{U}_3\text{O}_8$  in blank. Determine amount of  $\text{U}_3\text{O}_8$  present from a transmittancy-concentration curve obtained by developing the color with known amount of uranium present.

COLORIMETRIC DETERMINATION OF  
 $U_3O_8$  IN PHOSPHATES

Weigh sufficient sample to contain 200 to 600 micrograms of  $U_3O_8$ . Transfer to a 250 ml beaker. Add 40 ml nitric acid (1 + 1). Boil for about 5 minutes, dilute with water and filter through a #42 Whatman filter paper. Reserve the filtrate. Ignite the paper and residue in a platinum crucible until the filter paper is destroyed. Cool the crucible, moisten the residue with 2 to 4 drops of sulfuric acid (1 + 1). Place the crucible on a hot plate, fill  $2/3$  full of hydrofluoric acid and evaporate to dryness.

Fuse the hydrofluoric acid residue with 5 g of sodium carbonate. Dissolve the cool melt in 40 ml of nitric acid (1 + 1) and combine with the filtrate from the original nitric acid treatment.

Add 25 mg of ferric nitrate to the combined filtrates to act as a carrier for the  $R_2O_3$  group. Heat the solution almost to boiling, and while still hot, precipitate the  $R_2O_3$  group with ammonium hydroxide (1 + 1). Allow the precipitate to settle and then filter the solution through a Whatman #42 filter paper. Test the filtrate for sulfate ion by transferring a portion to a test tube, acidifying with HCl and adding barium chloride (10%). If sulfate ion is present, as shown by the  $BaSO_4$  precipitate, dissolve the hydroxide from the paper with hot nitric acid (1 + 1), and repeat the ammonium hydroxide precipitate as many times as is necessary to obtain a negative test for the sulfate ion in the filtrate.

Dissolve the final ammonium hydroxide precipitate with hot nitric acid (1 + 1) and evaporate the solution almost to dryness on

the steam bath and add 40 ml of nitric acid (1 + 5). To the solution add 5 g ferric nitrate to complex the phosphates present, and enough ammonium nitrate to saturate the solution.

Transfer the nitric acid solution of the sample saturated with ammonium nitrate to Part A of the continuous extractor. Take care that no sample is lost through the sidearm. A long stem funnel or stirring rod must be used. Some solid ammonium nitrate should be present.

Pour ethyl ether into the thistle tube portion of the frit, part B of the extractor. The ether should tend to form a column, place part B in position with the frit end at the bottom.

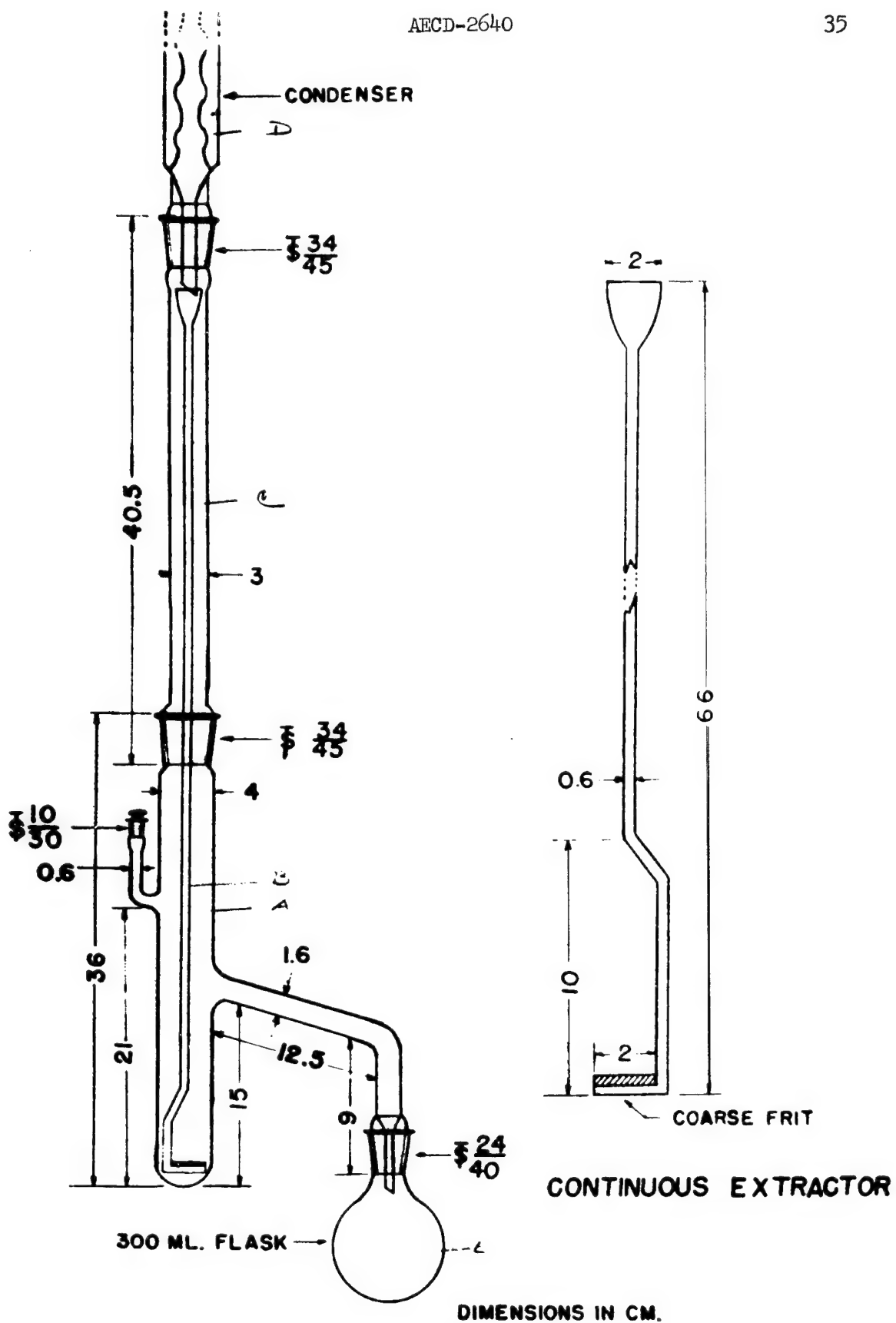
Fill the receiving flask, (E), 1/3 full with water and add enough ether to form a layer 1 inch thick. Attach the receiving flask (E) to the extractor (part A) as in the figure. Be sure the glass stopper is in place in the small sidearm on Part A.

Attach the column C to part A as in the figure. This part may be warmed in hot water to hasten the start of the extraction.

Attach the condenser (part D) as in the figure and pass cold water through it continuously. If more than one extractor is being used, the condensers may be cooled in series (up through four extractors).

Place a hot water bath on a round hot plate set at low heat, around the receiving flask (E).

After a short time the ether from flask E will reflux from condenser D and drip into the thistle tube at the top of Part B. The ether will build up a column and begin to pass through the glass frit in tiny bubbles. The ether layer in part A will overflow into the receiving flask E. Operate as rapidly as possible without causing the ether in the receiving flask to boil.



After about 15 minutes, raise the column C and stir the water solution in part A by raising and lowering part B. Repeat every 15 minutes.

If any precipitates form, add 5 ml of concentrated  $\text{HNO}_3$  saturated with  $\text{NH}_4\text{NO}_3$  through the small sidearm opening in Part A.

At the end of 90 minutes remove the water bath and allow the flask E to cool. Transfer the contents of the flask to a 400 ml beaker. Rinse the flask with most of the ether layer from extractor part A and add to the beaker. Wash the flask once with water, adding the wash to the beaker, and then place in the steam bath and evaporate to dryness.

Wash down the side of the beaker with 15 ml of nitric acid (1 + 9), add about 10 glass beads, 1 ml of perchloric acid (70%) and 2 ml of sulfuric acid. Cover with a speedyvap and heat until sulfur trioxide fumes are evolved. Continue the heating until the sulfuric acid refluxes half-way up the side of the beaker. Cool, rinse down the side of the beaker and wash glass with not more than 30 ml water. Make the solution slightly alkaline with sodium hydroxide (1 + 1), and add 1 ml of 10% sodium peroxide solution. Transfer to a 50 ml volumetric flask. Add 2.5 ml sodium hydroxide (1 + 1) and dilute to volume with water. Transfer the water solution back to the original beaker and filter the solution through a dry #40 Whatman filter paper into a dry Erlenmeyer flask.

Read percent transmission with a Beckman spectrophotometer in 10 cm cells at a wave length of 390 mμ and a slit width of .03 mm. Read samples against water and subtract amount of  $\text{U}_3\text{O}_8$  in blank. Determine amount of  $\text{U}_3\text{O}_8$  present from a transmittancy - concentration curve obtained by developing the color with known amount of uranium present.

DETERMINATION OF URANIUM IN LOW GRADE ORES AND SANDS  
FLUORIMETRIC METHODS.

The methods described here have been extensively used for the quantitative analysis of traces of uranium in low grade ores, sands, soils and a variety of other materials. The yellow fluorescence of uranium in fused sodium fluoride under ultraviolet light is intense and reproducible. A Hanovia type mercury vapor lamp which produces light rich in the 3650 Å mercury line is suitable for excitation and preferable to shorter wave length sources which may excite interfering fluorescence. Phosphor discs are made from a fusion mixture of sodium fluoride and sodium and potassium carbonates which has the advantage of a lower melting temperature than sodium fluoride alone. Corning glass filters are used to isolate the desired exciting wavelengths and to eliminate reflected ultraviolet light from the fluorescent light. Interferences from foreign ions such as iron, chromium, manganese and copper, which inhibit the fluorescence are eliminated by extraction of the uranyl nitrate with ethyl acetate or by the dilution technique which relies on reducing the quenching elements by the use of a sufficiently small sample for analysis.

I. Apparatus. The apparatus is identical to the Model R Fluorimeter\* with the exception that a special photomultiplier search unit may, depending on the procedure used, replace the search unit described for this Model. The sensitivity of the instrument, when

\* Report C-4.381.4, March 11, 1946, Charles F. Coleman.



provided with the photomultiplier search unit, is stated to be more than 1,000 times higher than the sensitivity of the Photovolt standard Model 512 search unit.

A systematic diagram of the instrument is shown in Figure I. The construction drawings of the fluorimeter and the principal accessories are reproductions of those in the aforementioned report. The accompanying photographs are of the instrument and other laboratory equipment mentioned in the procedures as used at the National Bureau of Standards. A set of instructions for operation of the Photovolt photometer is also included.

The errors caused by voltage changes, causing the incident light to change in intensity, are eliminated by use of a voltage stabilizer.

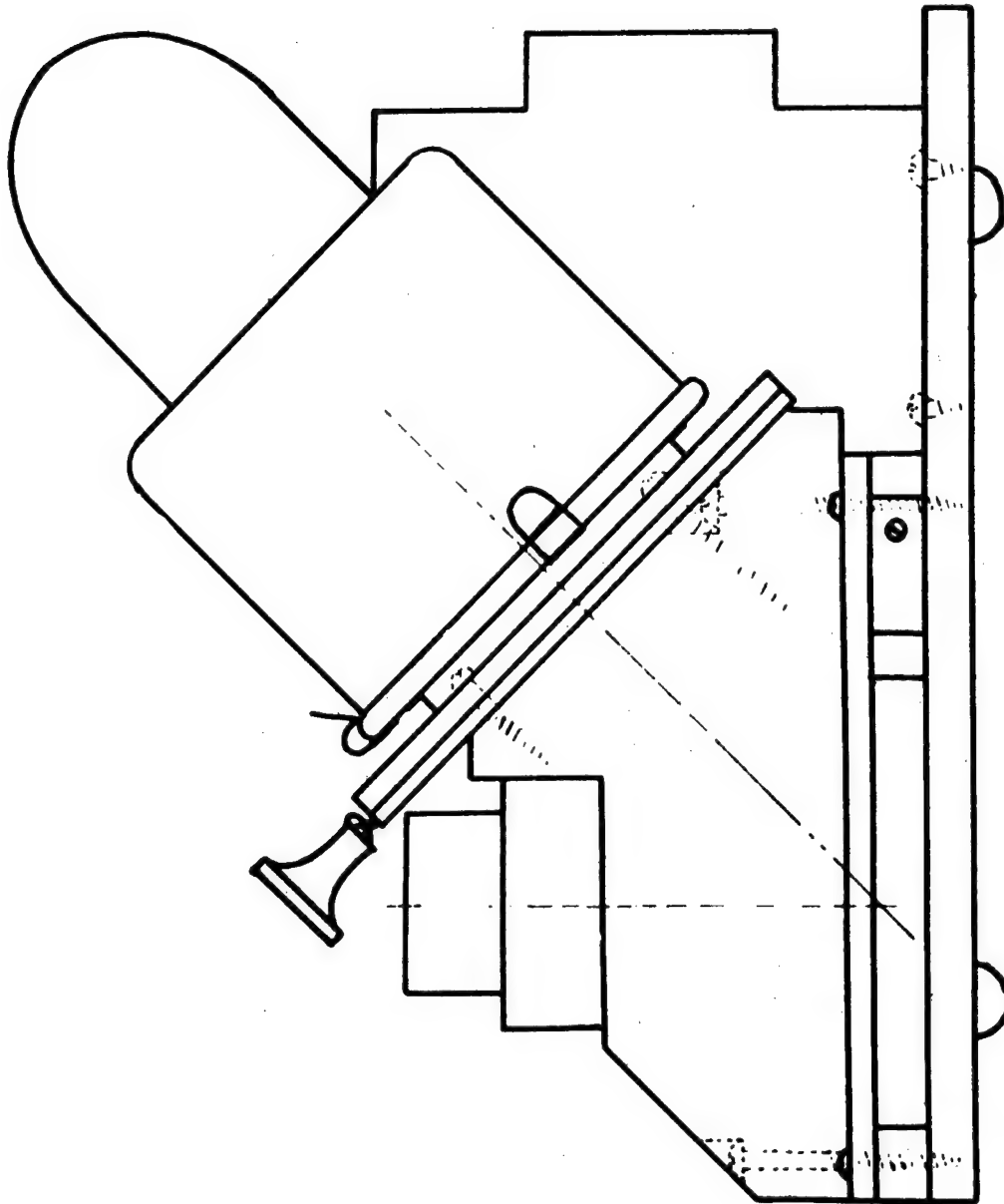
Materials Used in Construction of Model R Fluorimeter.

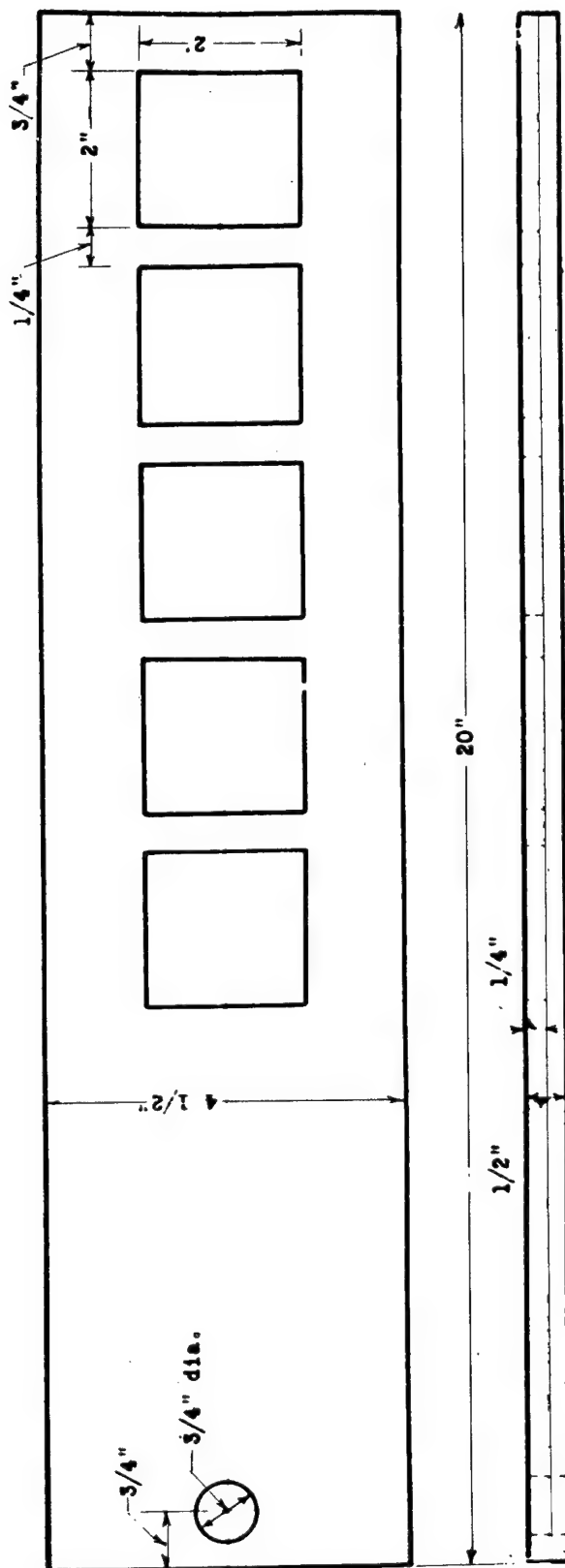
<u>Drawing No.</u>	<u>Quantity</u>	<u>Item</u>	<u>Type of Material</u>
I	1	Center Block	Wood
II	1	Slide	"
III	1	Photocell Holder	"
IV	1	Holder Support	"
V	1	Spring Guide	"
VI	1	Guide Bar	"
VII	1	End Bar	"
VIII	1	Transite Plate	Transite
IX	2	Guides	Brass
X	1	Spacer	"

<u>Drawing No.</u>	<u>Quantity</u>	<u>Item</u>	<u>Type of Material</u>
XI	1	Shutter	Brass
XII	1	Clip	"
XIII	1	Spring	Bronze or steel
XIV	1	Slide Cover	Wood
XV	1	Base	"
XVI	1	U.V. Filter, Corning # 587 (365 mu)	Glass
XVII	1	Yellow Filter, Corning # 3486 (530 mu and above)	"
XVIII	1	Blue Filter, Corning # 9780 (mainly below 600 mu)"	
	4	1/2 " #6 RH machine screws	
	2	3/4 " " " " "	
	2	3/4 " " " wood screws	
	13	1 1/4 " " " " "	
	10	1/2 " " FH " "	
	8	1 " " " " "	
	4	1/2 " #8 RH " "	
	4	2 1/2 " " " " "	
	1 Photometer: Photovolt Model 512 with photocell		
	1 Photovolt Photomultiplier Search Unit		
	Photovolt Corporation, 95 Madison Avenue, New York 16, New York		
	1 Ultraviolet Lamp: Hanovia Type 16200 with holder for 3 1/4" filter. Hanovia Chem. Co., Newark, N.J.		

QuantityItem

- 1 Sola Constant Voltage Transformer: Cat. No.30213  
Volts 115, Amps. 2.5, Freq. 60, Pri. Volts 95 to  
125. Sola Electric Co., Chicago,Ill.



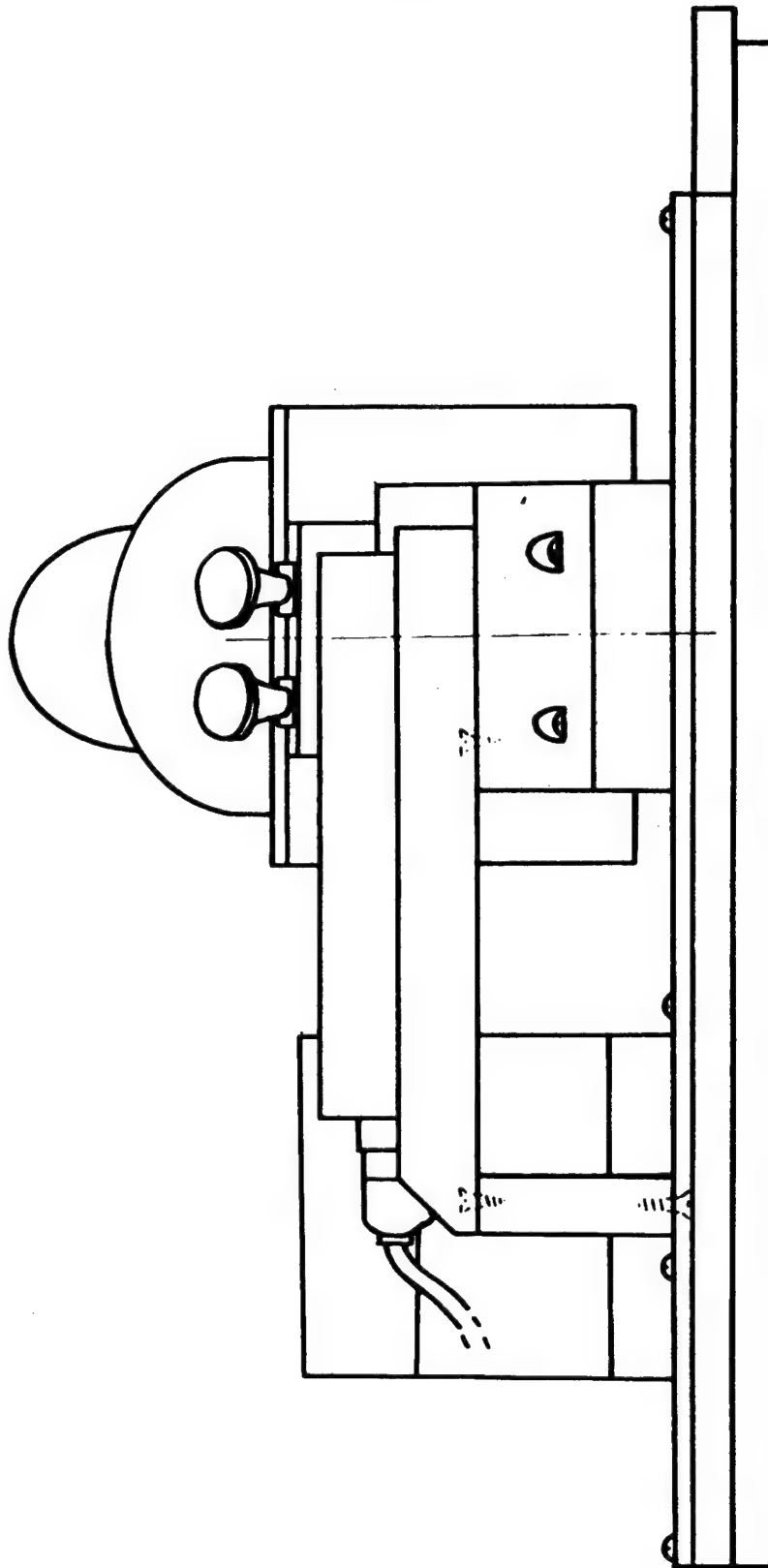


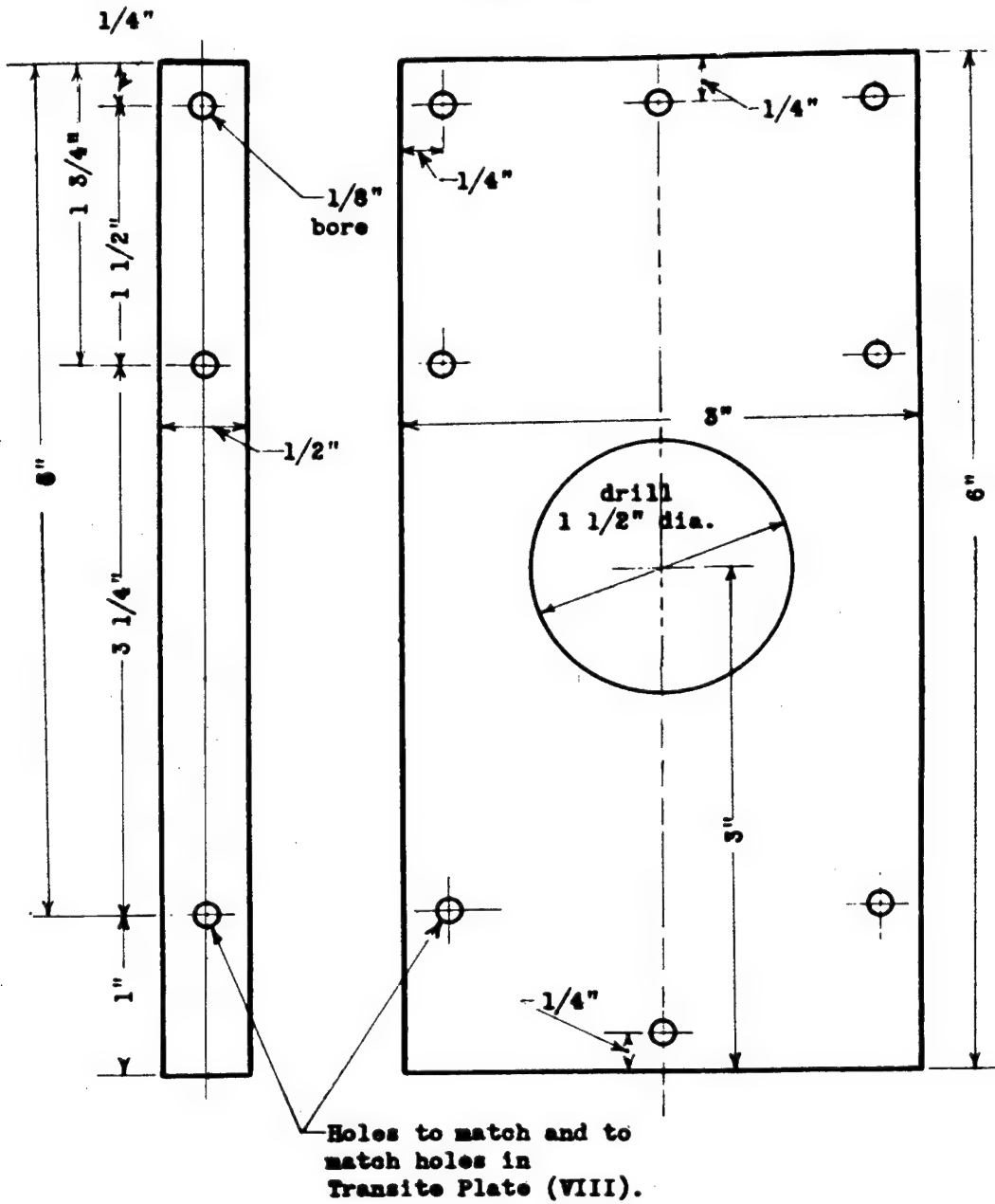
Glue together two layers of 1/4"-plywood after cutting square holes in upper piece.

one piece  
paint flat black

11. SLIDE

(Scale: 1/2)





0.050" brass  
two pieces

IX. GUIDES

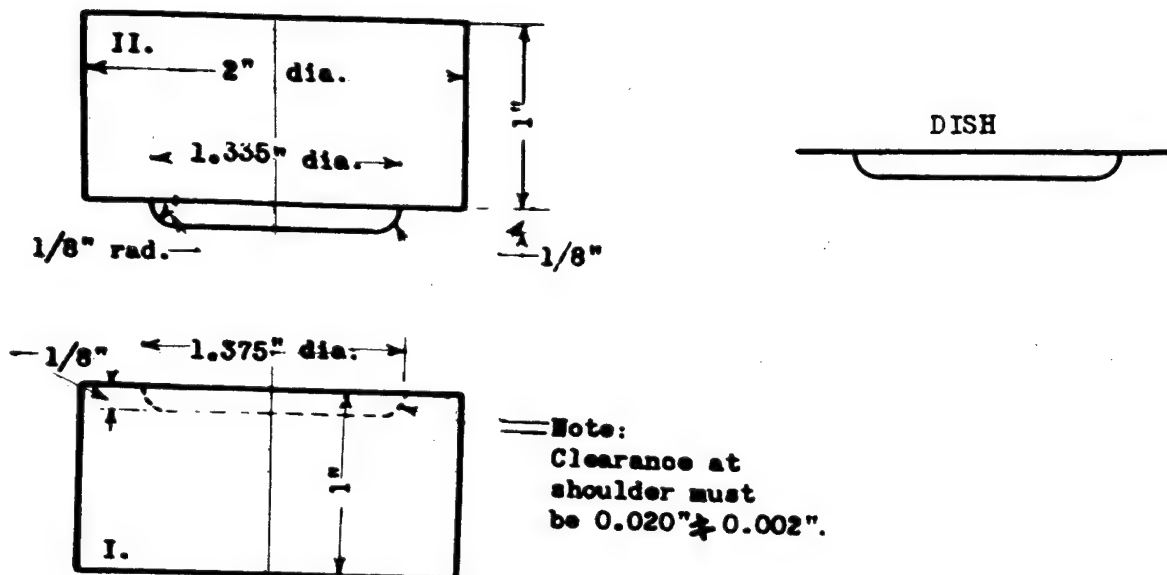
0.030" brass  
one piece

X. SPACERS

(Scale: 1)

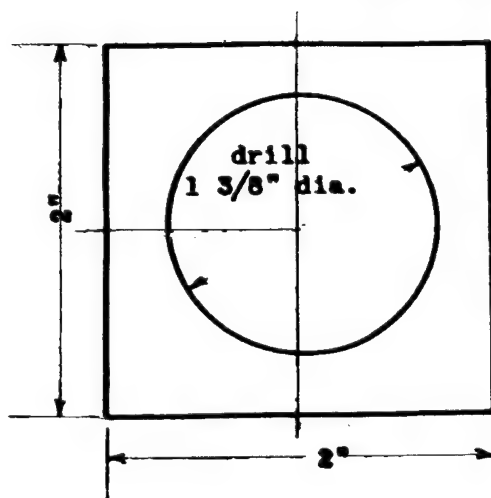
DIES FOR FLUORESCENCE DISHES

steel



FLUORESCENCE DISHES

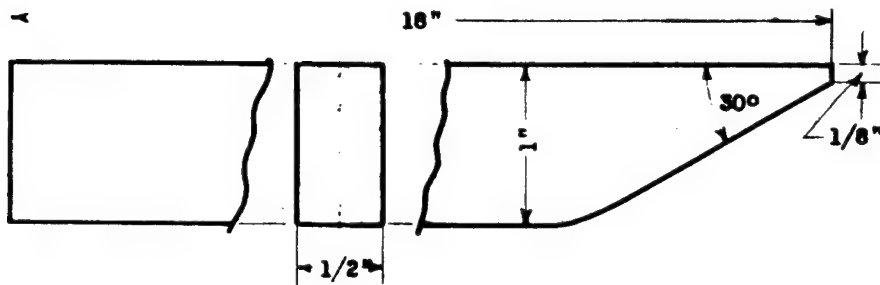
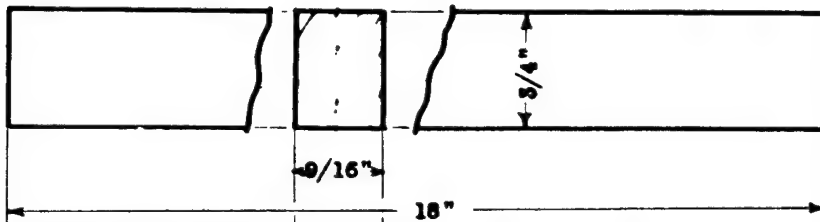
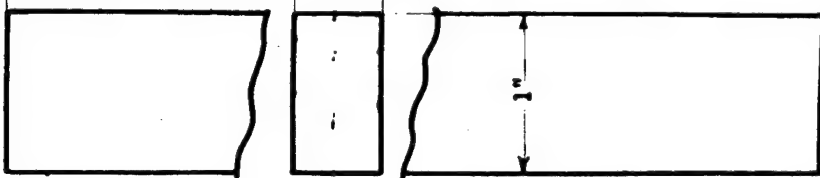
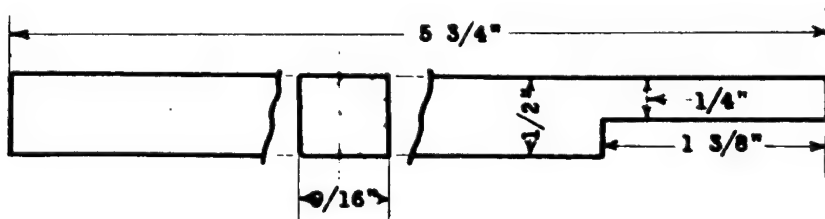
0.020" gold



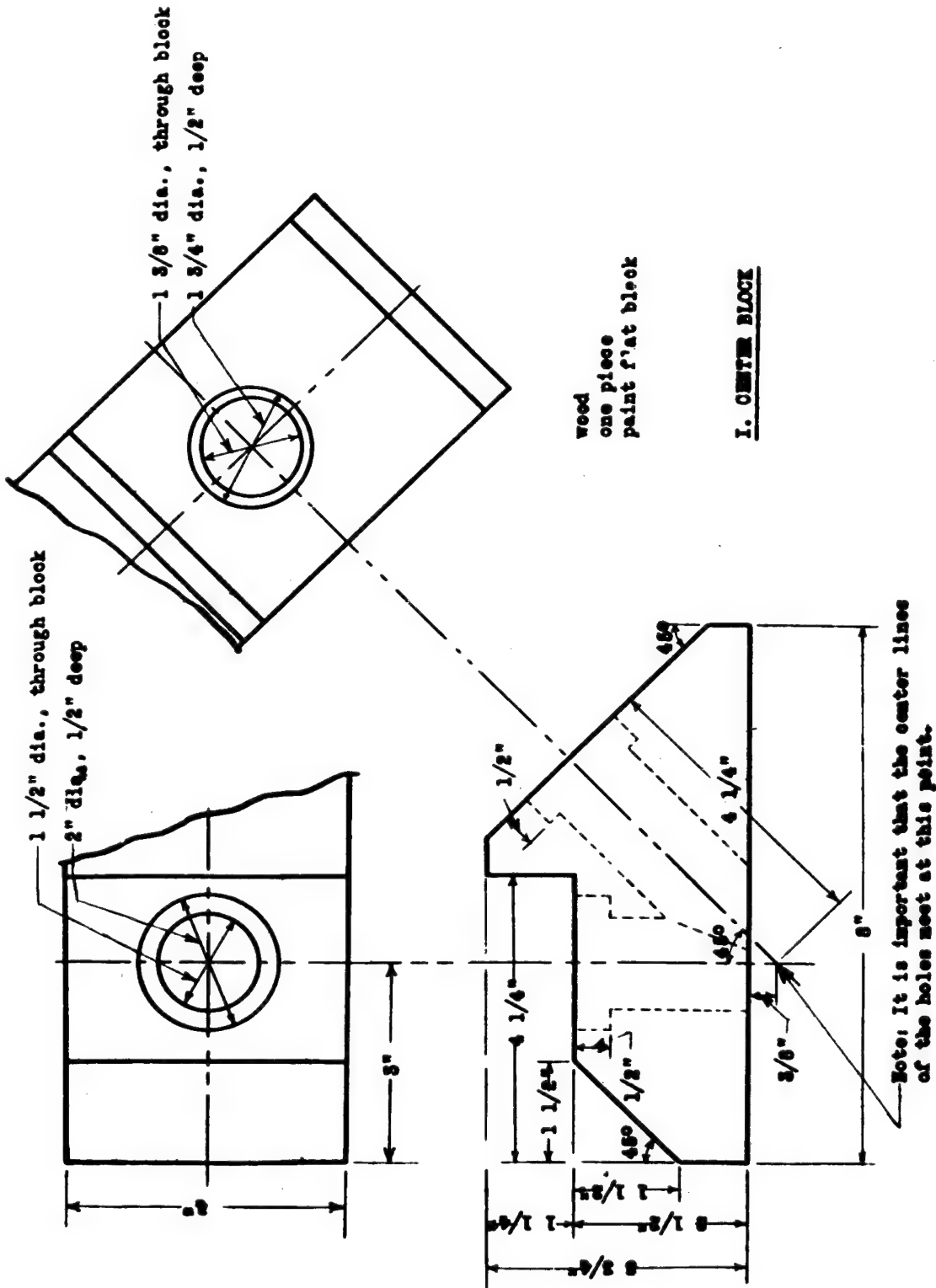
ADAPTER to hold dishes in  
fluorimeter slide

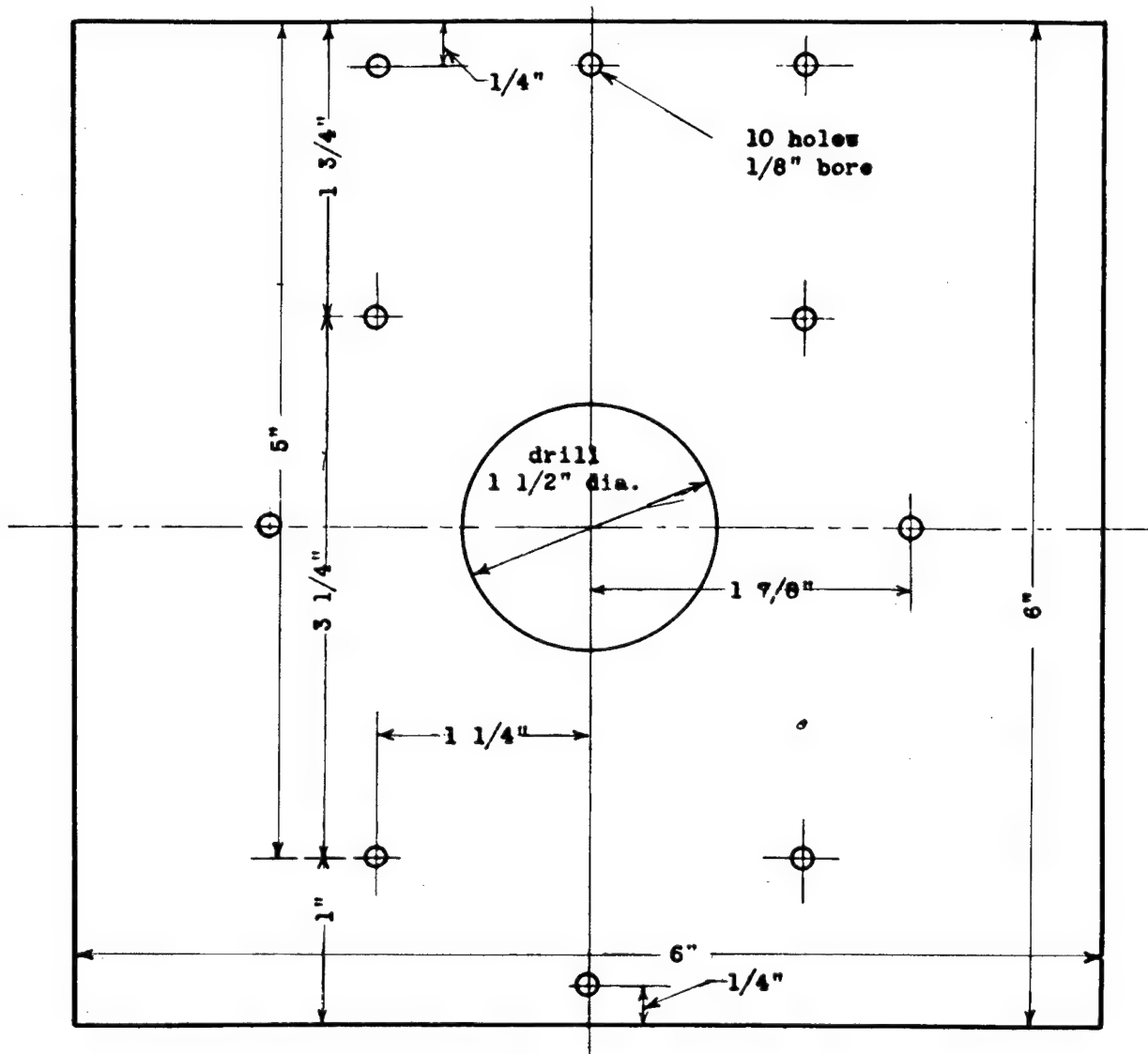
3/16" presswood; sand to fit.  
paint with India ink



V. SPRING GUIDEVI. GUIDE BARVI'. GUIDE BARVII. END BAR

wood  
one piece each  
paint flat black

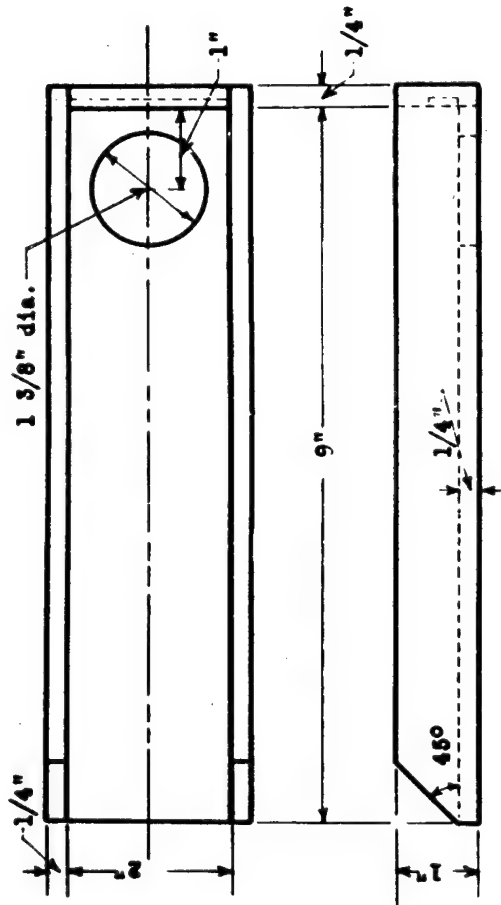




1/4\" transite  
one piece  
paint flat black

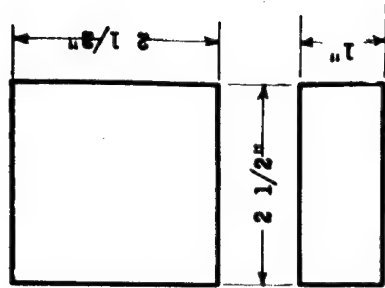
VIII. TRANSITE PLATE

(Scale: 1)



wood  
one piece  
paint flat black

III. PHOTOCELL HOLDER

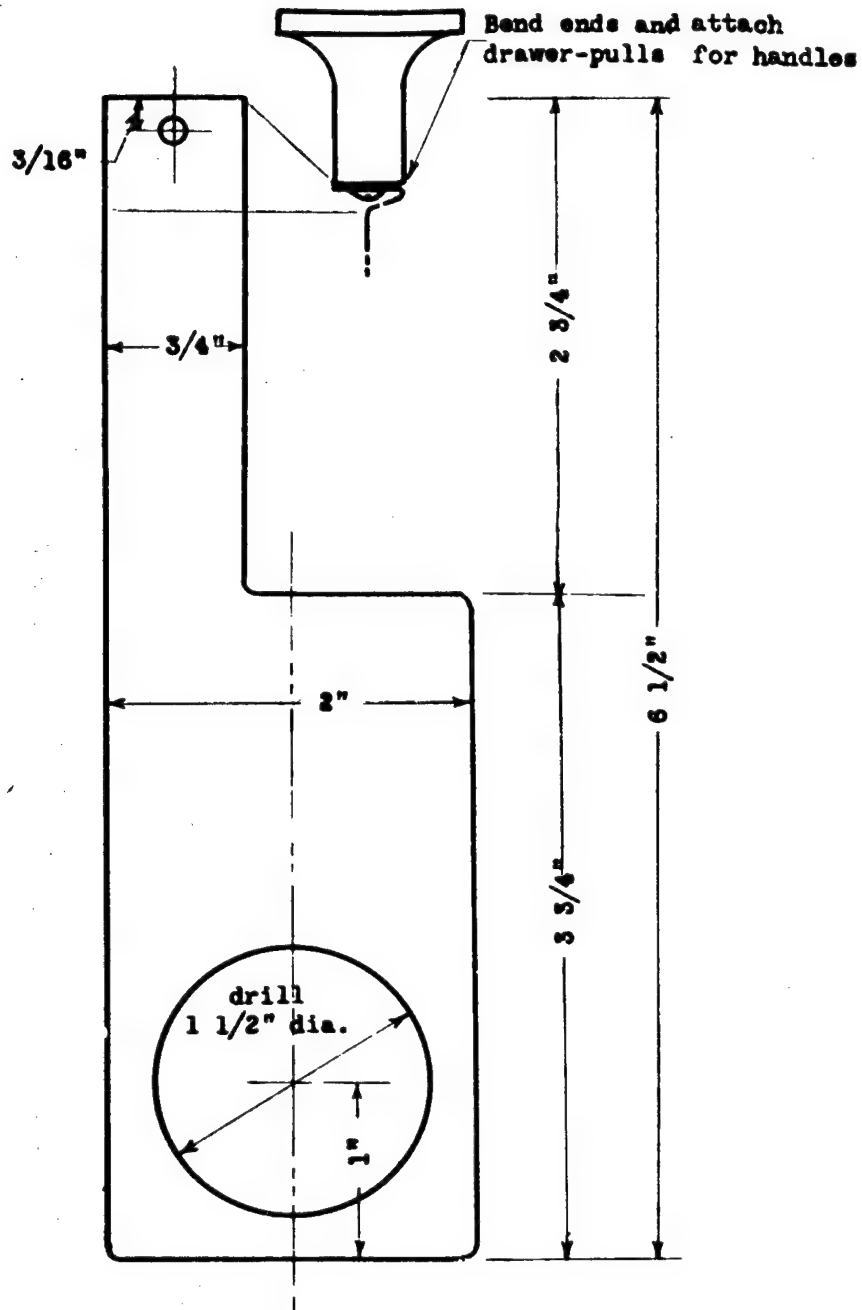


wood  
one piece  
paint flat black

IV. HOLDER SUPPORT

(Scale: 1/2)

AECD-2640



0.030" brass  
one piece

XI. SHUTTER

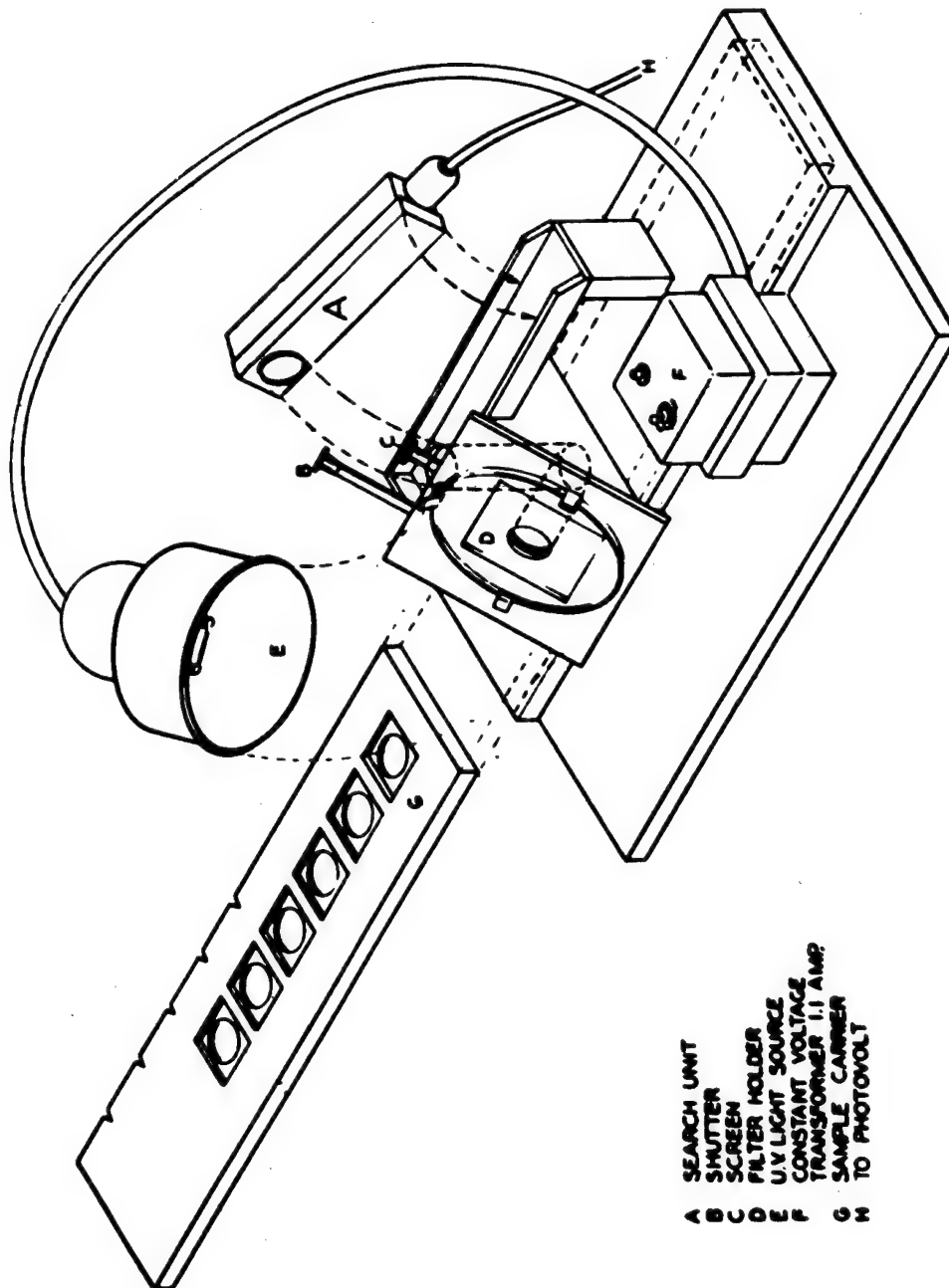
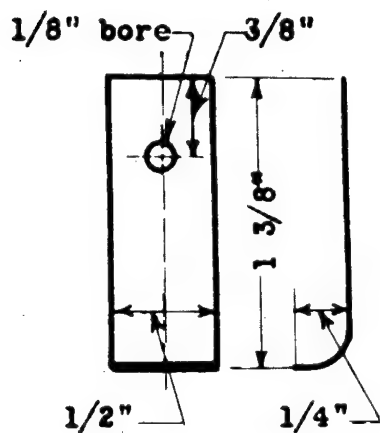
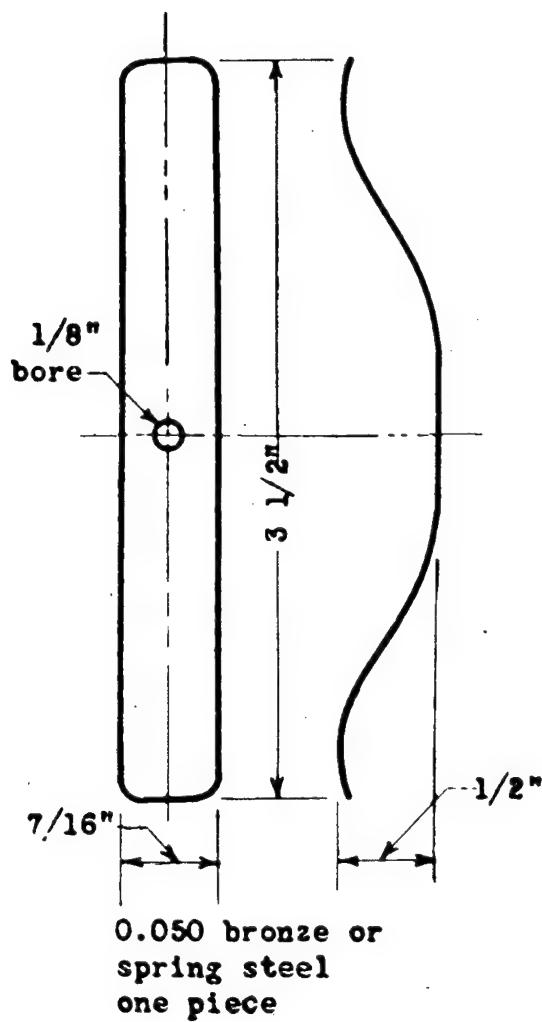


FIGURE I



0.030" brass  
one piece

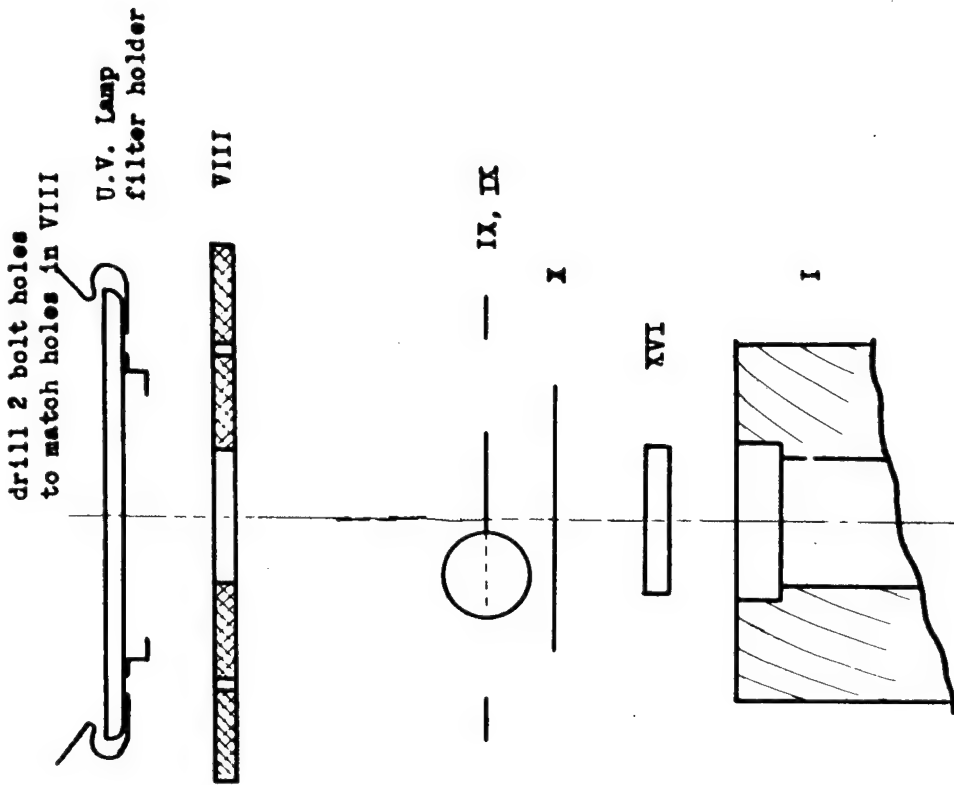
### XII. CLIP



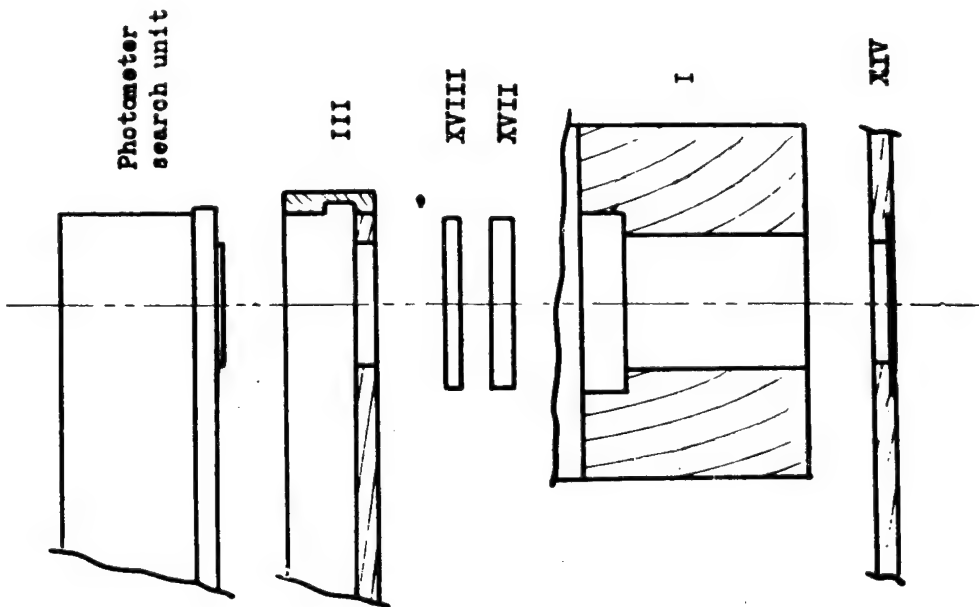
0.050 bronze or  
spring steel  
one piece

### XIII. SPRING

(Scale: 1)

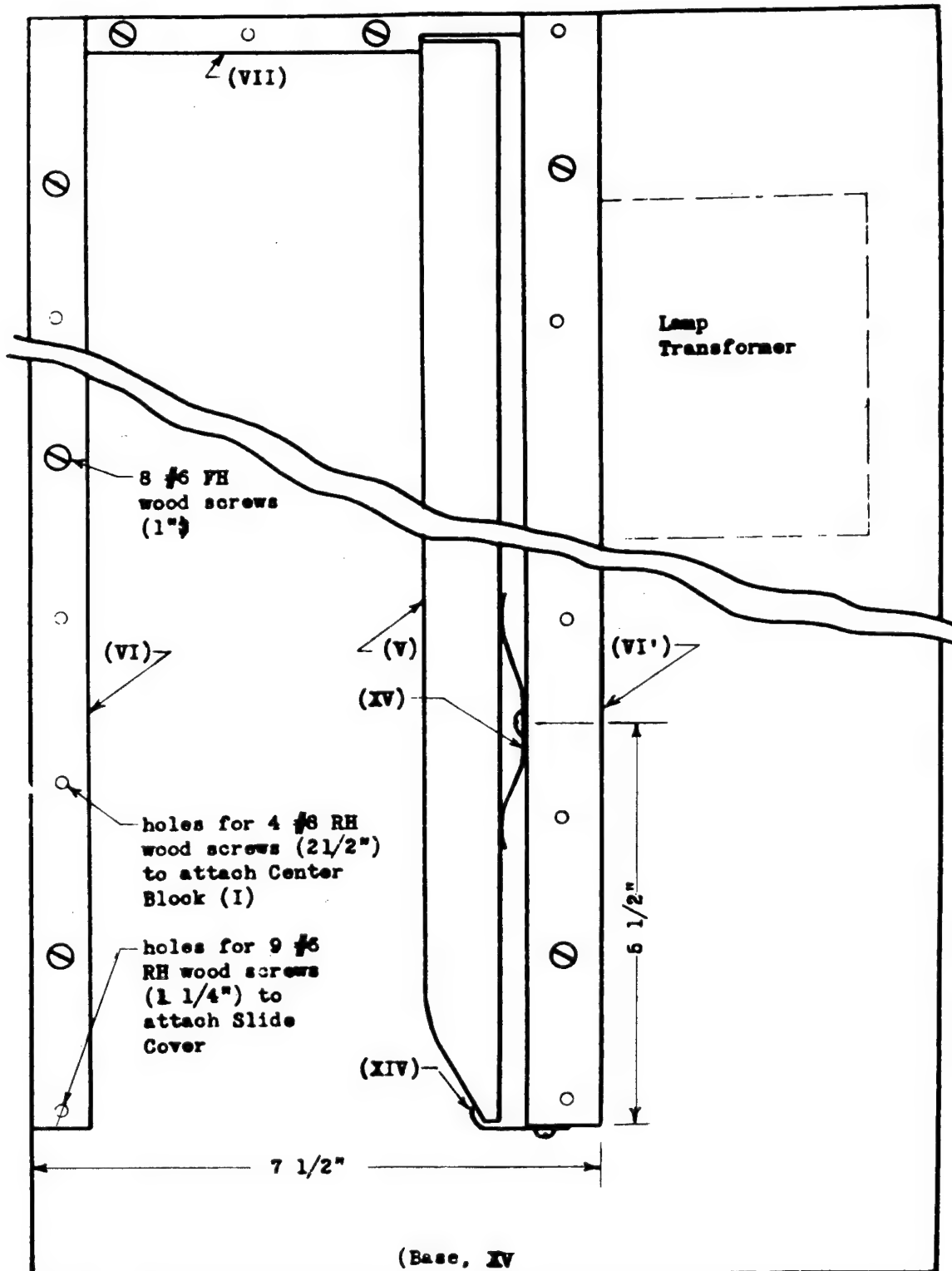


Attach Filter Holder to Transite Plate (VIII) with 2 #6 RH machine screws, Guides and Spacers (IX and X) to (VIII) with 4 #6 RH machine screws (1/2"), and (VIII) through (IX) and (X) to Center Block (I) with 4 #6 RH (wood) screws (1 1/4").



Attach (XVI) to Center Block (I) with 4 #6 FH screws (1/2"), Photometer Holder (II) to (I) with 2 #6 FH screws (1/2"), and (I) through Cover and guide bars to base with 4 #6 RH screws (2 1/2").





XV. BASE

3/4" plywood, 12" x 20"  
one piece  
paint flat black

XVI. U.V. FILTER

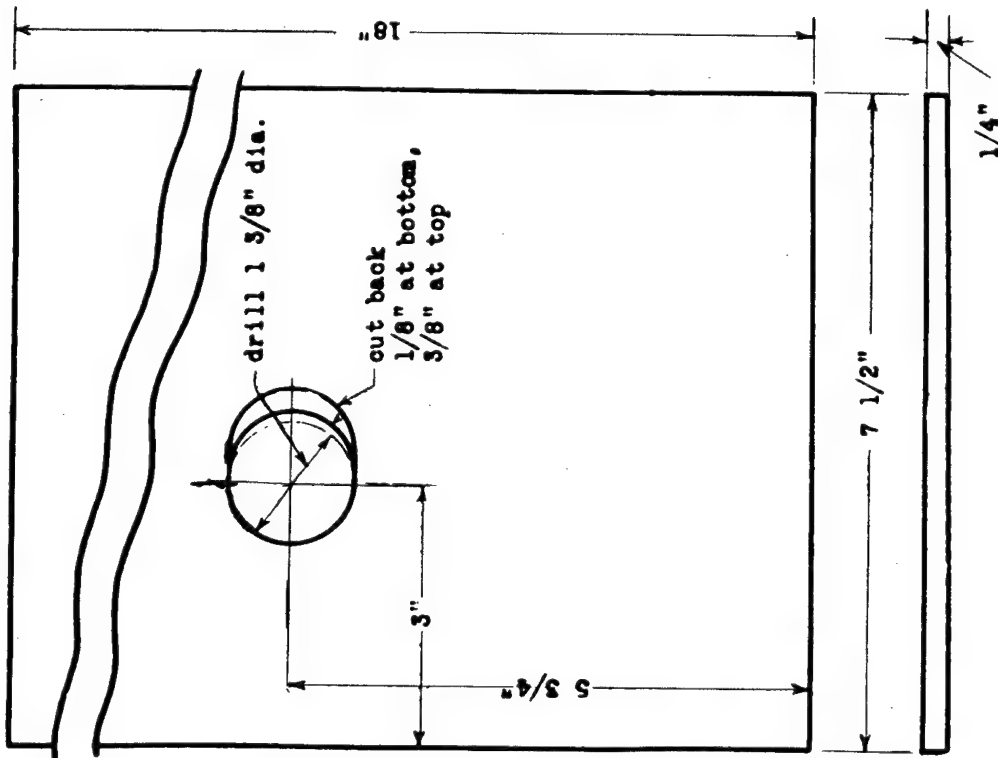
Corning #587 (365 mμ)  
1 11/16" dia. x 1/4"  
one piece

XVII. YELLOW FILTER

Corning #3486  
(530 mμ and above)  
1 15/16" dia. x 1/4"  
one piece

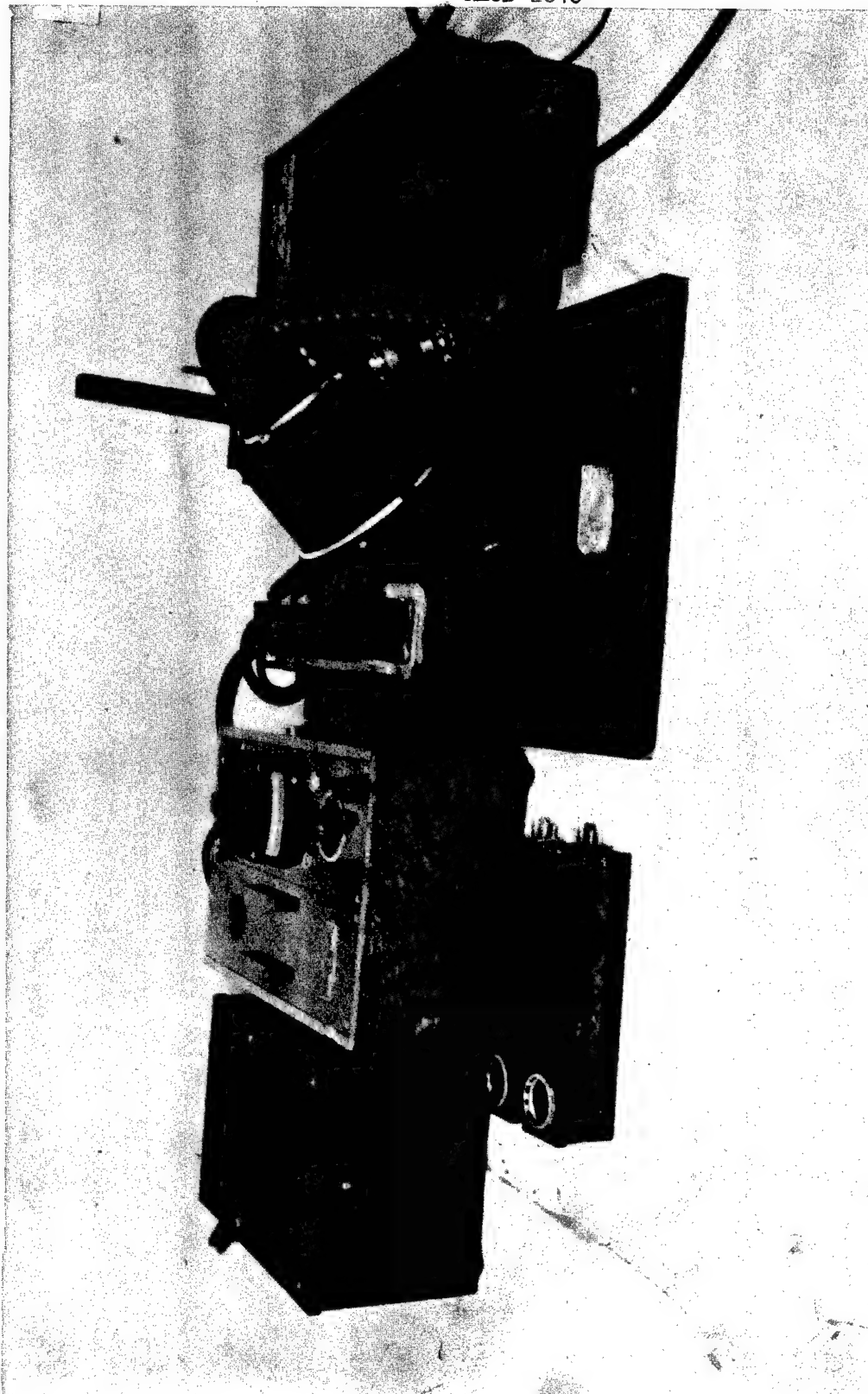
XVIII. BLUE FILTER

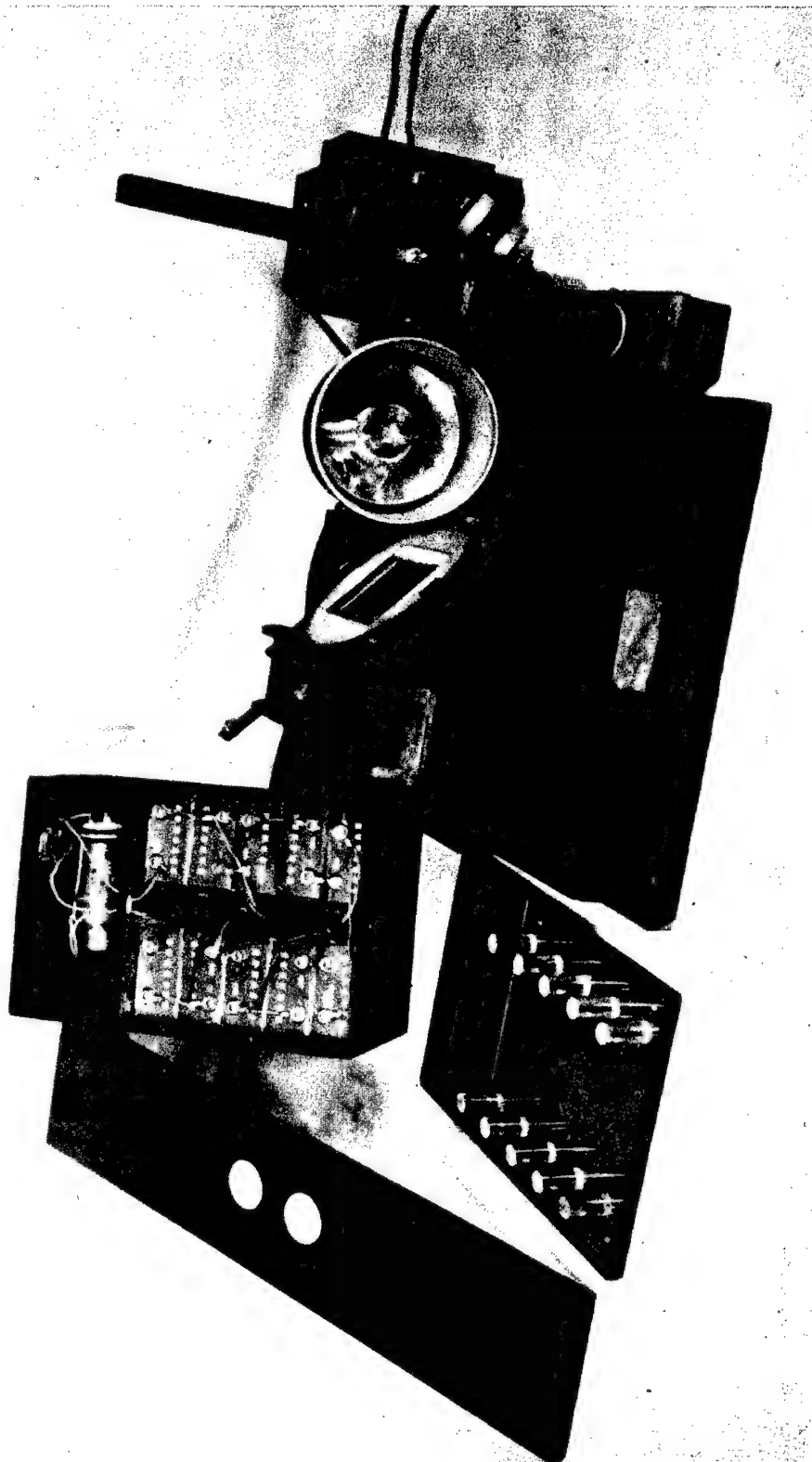
Corning #9780  
(mainly below 600 mμ)  
1 15/16" dia. x 1/8"  
one piece

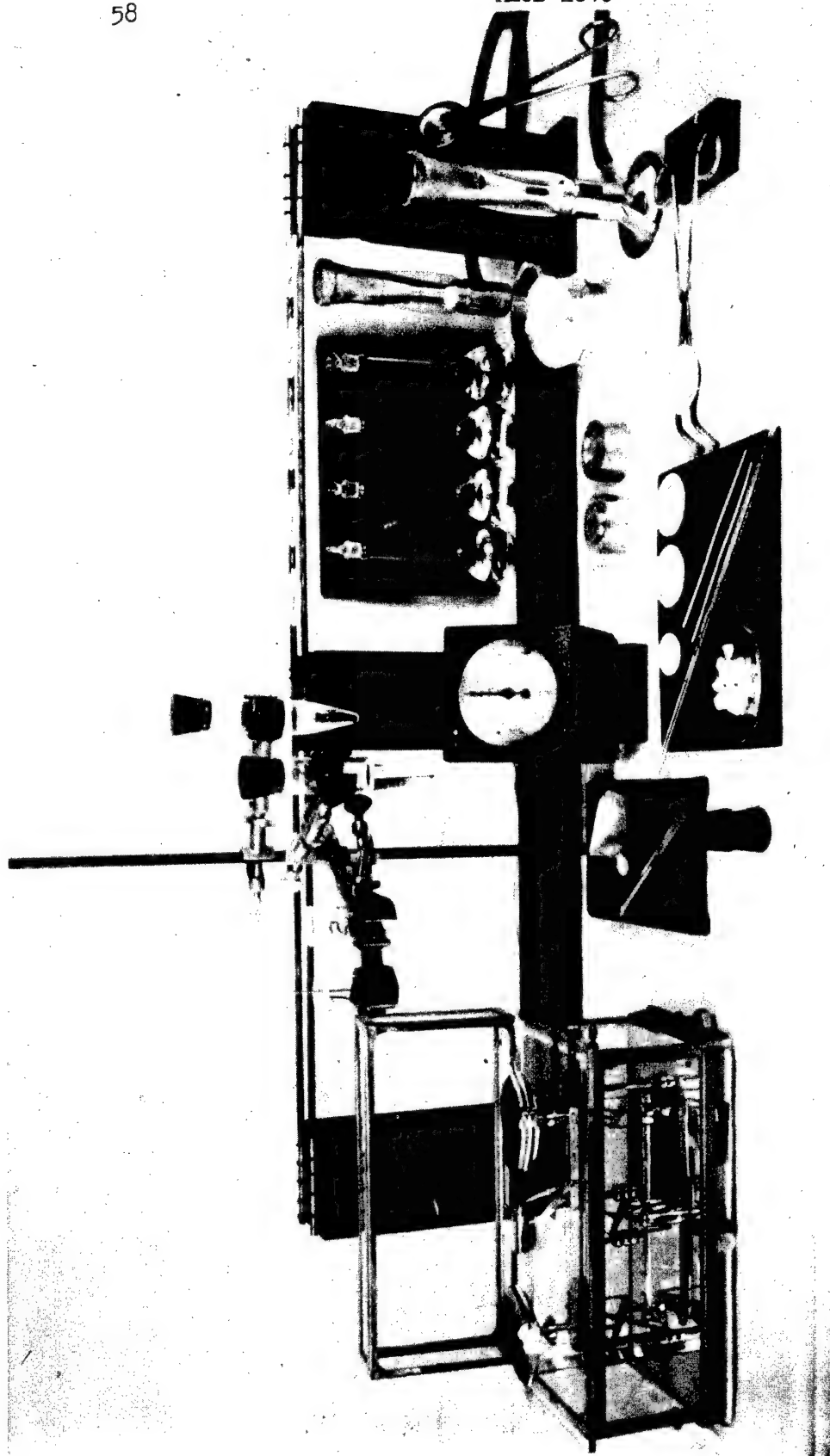


1/4" plywood  
one piece  
paint flat black

XIV. SLIDE COVER







## II. Ethyl Acetate Extraction Method.

Solution of Samples. Mix thoroughly a finely ground accurately weighed sample (0.1000 or 0.2000 grams) of the ore containing 10 to 50 micrograms of uranium with 3.00 grams of  $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$  (1:2 fusion mixture) in a 100 ml. platinum dish. Fuse the sample over a blast Meker burner. Decompose the carbonates by adding 10 ml. of water, covering the dish with a watch glass and forcing 5 ml. of  $\text{H}_2\text{SO}_4$  (1+1) under the watch glass from a pipette. After the reaction has ceased, remove the watch glass, and wash back into the solution any adhering liquid. Add 10 ml. of 48% hydrofluoric acid and evaporate the solution as far as possible on a steam bath. Transfer the sample to a hot plate and heat until fumes evolve. When fuming begins, remove the sample and fuse over a Meker burner. Apply the heat carefully until the clear liquid solidifies. Cool and add 5 ml. of concentrated  $\text{HNO}_3$  and 30 to 35 ml. of water. Place the sample on a steam bath and stir occasionally with a glass rod until solution is complete. Cool, transfer to a 100 ml. volumetric flask and make to volume.

Preparation of Blanks and Standards. Prepare a blank by carrying 3.00 grams of the carbonates through the procedure as for solution of the sample. Prepare three standards by adding 2, 4 and 8 ml. of a standard uranium solution, which contains 5 micrograms of uranium per 1 ml., to three respective 100 ml. platinum dishes. Evaporate the solutions to dryness and carry through the same procedure as for the sample.

Extraction with Ethyl Acetate. Pipet 10 ml. aliquots of the sample, blank and standards into 50 ml. pyrex glass graduated centrifuge tubes. Add 1 ml. of an aluminum nitrate solution, which contains 20 milligrams of  $Al^{+++}$  ion, to each tube. Adjust the volumes to 35 or 40 ml. and precipitate the hydroxides with excess ammonium hydroxide. Use platinum rods of 2 mm. in diameter and 150 mm. in length to stir the solutions during precipitation. Centrifuge the samples and discard the liquid portions. Dissolve the hydroxides with 1 or 2 ml. of concentrated  $HNO_3$  and again adjust the volumes to 35 or 40 ml. Reprecipitate the hydroxides with excess ammonium hydroxide. Centrifuge and discard the liquid portions. The second precipitation is necessary to free the sample of any sulfate ion, which, if present in more than small quantities, interferes with the extraction of uranium. Dissolve the precipitate with 1 ml. of  $HNO_3$  (1+1) and add 9.0 grams of  $Mg(NO_3)_2 \cdot 6H_2O$  crystals to each tube. Adjust the volumes to 10.0 ml. with water and dissolve the salts by heating gently over a Meker burner. Mix the solution thoroughly and allow to cool. If necessary readjust the volumes to 10.0 ml. Add exactly 5.00 ml. of ethyl acetate to each tube. Stopper the tubes with #6 rubber stoppers\* and shake vigorously for 2 minutes. Centrifuge the

\*Rubber stoppers must generally be cleaned prior to use, since a yellow substance, probably sulfur, extracts from the rubber. To clean, place stoppers in a jar, cover with ethyl acetate, shake 5 to 10 minutes and allow to soak overnight. Remove and shake the stoppers in fresh ethyl acetate for 5 minutes, remove and use.

samples with stoppers intact. Draw off 1.00 ml. aliquots and transfer to gold dishes resting on a stand having two parallel nichrome rods. In a draft free room, ignite a toothpick and bring the flame to within 1/2 to 1/4 inch of the ethyl acetate surface and when the acetate vapor ignites spontaneously, quickly withdraw the flame. Pipet and ignite each sample singly. After the acetate has burned off, ignite any carbon residue by placing the flame of a Meker burner under the gold dish.

Preparation of Flux and Phosphor. The preparation of the flux is as follows: Weigh 24.0 grams of  $\text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3$  (1:2 fusion mixture) and 6.0 grams of NaF into a 100 ml. platinum dish. (It is understood that all dishes and glassware used throughout the procedure are thoroughly clean). Mix the salts thoroughly and fuse over a Meker burner. When a clear homogeneous solution results, quickly place the dish in a shallow pan of cold water. Transfer the melt, which is easily removed, to a clean mortar and break up into small pieces about 1/4 inch square by gently tapping with a pestle. The flux can be kept indefinitely in an oven at 110°C.

Prepare the phosphor by weighing out 2.50 grams of the flux on a small torsion balance and transfer to the gold dish which contains the uranium. Clasp the bowl of the gold dish with a pair of nichrome crucible tongs and fuse the salts over the full flame of a Meker burner for exactly 2 minutes. About 1 minute is required for the complete melting of the flux and during the remaining time slightly tilt the dish and roll the melt around the rim surface of



the dish. At the end of the time period drain the melt back into the bowl of the dish. Place the tongs, with the gold dish, at rest in a level position and allow the melt to solidify undisturbed. When cool, remove the discs from the gold dishes.

Reading the Phosphors. Use only two circular recesses of the fluorimeter slide, one for the blank and the other for the standards and the samples. Insert the blank in one recess and the high standard, prepared from the solution containing 40 micrograms of uranium, in the other recess. By manipulation of the shutter and the wide range zero screw, adjust the light intensity so as to have the high standard read 80 on the Lo scale and the blank 0 on the Lo scale. Replace the high standard by the other two standards, which will read if properly prepared, respectively 20 and 40 on the Lo scale. Readings should not vary more than 1 or 2 divisions on the galvanometer from the expected readings. After adjustment of the instrument for the standards, read the samples. Keep a check on the zero setting of the blank and readjust when necessary. A complete set of 8 samples can be rapidly read before any drift is noticed in the zero setting. Calculate the percentage uranium from the standard readings.

The standard samples need not be prepared each day if there is no change in the reagents. The standards appear to keep well for about three or four days if stored in Petri dishes in an oven maintained at  $110^{\circ}$  -  $115^{\circ}$  C.

### III. Direct Method.

#### Solution of Sample

Same as for Ethyl Acetate Extraction Method.

#### Preparation of Blanks and Standards

Same as for Ethyl Acetate Extraction Method.

#### Method

Depending upon interfering ion concentration, analysis are made using 1.00 ml. or 0.075 ml. aliquots from the standards and samples containing 10 to 50 micrograms of uranium per 100 ml. Pipet the aliquots on to the gold dishes and evaporate to dryness under an infra-red lamp. Prepare and read the phosphor discs as directed in the Extraction Method.

Prepare new phosphor standards each day by evaporation of the desired aliquot from the originally prepared standard solutions. It is only necessary to prepare entirely new standard solutions where there is a change in the reagents and then only one standard solution need be prepared and checked against the older solutions. If there is a noticeable change due to the reagents, prepare an entirely new set of standard and blanks.

Make a pipette, used for measuring 0.075 ml. aliquots, from 1/2 cm. capillary tubing of 1/2 mm. bore. Draw the tubing out about 5 cm. to converge to a point of 1 to 1 1/2 mm. and a bore of 0.1 to 0.2 mm. Overall length is 40 cm. Make a scratch on the tubing 30 cm. from the converging end. The volume can be determined by weighing the water delivered. In actual work it is not necessary to know the volume delivered as the same aliquot is taken

from both standards and samples. In taking aliquots entirely empty the pipette by blowing the last drops onto the gold dish. Clean the pipette with  $\text{HNO}_3$  acid, water and acetone.

IV. Procedure for Instrument with Standard Model 512 Search Unit.

Prepare the sample, blank and standard solutions identically with the foregoing procedures. Pipet 40 ml. aliquots of sample, blank and standards into 50 ml. pyrex glass graduated centrifuge tubes. Add 1 ml. of an aluminum nitrate solution, which contains 20 milligrams of  $\text{Al}^{+++}$  ion, to each tube. Precipitate the hydroxides with excess ammonium hydroxide and follow the procedure as under Extraction with Ethyl Acetate and Preparation of Flux and Phosphor.

In reading the phosphors, open the shutter entirely and adjust the blank to read 0 on the Lo scale with the wide range zero screw. Read the standards and samples and calculate from the standard readings the percentage uranium. A standard curve may be drawn and used, however, it is advisable to run standards with the samples to avoid errors from changes in light intensity.

# PHOTOVOLT

## ELECTRONIC PHOTOMETER

### MODEL 512

## Operating Instructions

The instrument is furnished with an opaque disc in front of the phototube window. This disc must be removed in order to admit light. To remove the disc, unscrew the knurled metal ring.

### Operation, Step by Step

1. With main switch 1 on "OFF", set needle of galvanometer exactly on zero by means of mechanical zero adjustment knob 2 on top of galvanometer housing.
2. With main switch 1 on "ON" and with the search unit connected to the instrument, turn switch 3 to position "A". The galvanometer must show a deflection between 50 and 60. This checks the filament voltage on the amplifier tubes.
3. Turn switch 3 to position "B". The galvanometer must now show a deflection between 86 and 100. This checks the plate supply voltage.

It does not make any difference whether the phototube window is covered or uncovered during steps 1, 2, and 3.

4. After a warm-up period of approximately 5 minutes, cover up search unit so that no light whatever strikes the phototube. Keep phototube covered during steps 5 and 6.
5. Turn switch 3 to "LO". Set electrical zero adjustment knob 4 approximately to its middle position. If the needle is not near zero, use a screwdriver to set the needle approximately on zero with the wide-range zero adjustment 5.

The operation of the wide-range zero adjustment 5 is necessary only when the instrument is first taken into use or after it has been kept standing for a considerable period of time, also after changing from one search unit to another. In routine operation, it will mostly be sufficient to use knob 4 to set needle approximately on zero in step 5.

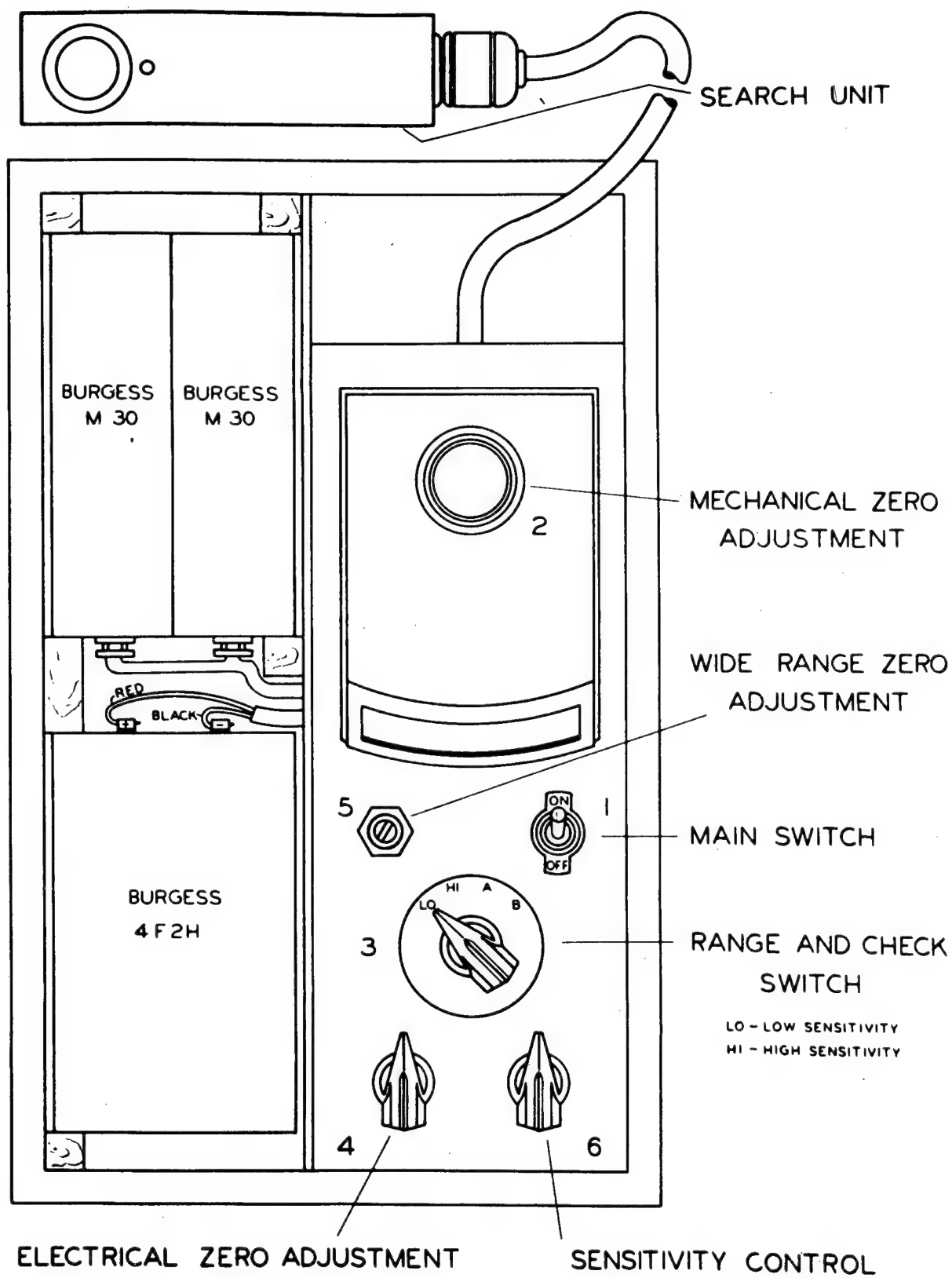
6. Turn switch 3 to "HI" and set needle exactly to zero with knob 4.

The instrument is now adjusted and ready for measurements. The zero adjustment according to step 6 should be checked from time to time by blocking off the light on the phototube. The ratio of 10:1 of the sensitivities in positions "HI" and "LO" of switch 3 holds true only if the mechanical zero adjustment of step 1 and the electrical zero adjustment of step 6 are accurately maintained.

### Notes

- a. The instrument reads in arbitrary light units. It is provided with a sensitivity control knob 6 which permits stepless control of the sensitivity. In the clockwise end position, the sensitivity is approximately 50% higher than in the counterclockwise end position. If the instrument is employed for the absolute evaluation of light values as, for instance, for exposure determination in photomicrography, all readings should be taken either in the one or the other end position of knob 6. On the other hand, if the purpose of the measurements is the determination of the ratio of two light values as, for instance, in density tests, the sensitivity control knob 6 may be found useful to set the needle on 100 or on some other even reading for the higher light value, so as to facilitate the calculation of the ratio.

- b. When the instrument is not in use, it is recommended to put the opaque disc back into the search unit window or to keep the phototube protected from light in some other way. Strong light striking the phototube window cannot result in any damage of the indicating meter, inasmuch as the circuit is completely self-protecting. However, a temporary instability may be caused by the phototube being struck by light so strong as to throw the needle far off scale.
- c. In checking the filament voltage of the amplifier tubes according to step 2, the needle may go to a value below 50. This shows that battery 4F2H must be replaced. Make sure that the search unit is securely connected during this test. It is a good plan to check the filament voltage when the instrument shows appreciable drift.
- d. The drain on the batteries supplying the plate voltage is so low that their life may be expected to be equal to their shelf life. Therefore, checking of this voltage according to step 3 need not be done except once in a great while. If step 3 results in an indication below 86, it is advisable to replace the two 45-volt batteries M 30. The two batteries are connected in parallel. In an emergency, one 45-volt battery is sufficient to operate the instrument.
- e. The batteries are accessible by taking off the left-hand panel after removing the six screws along the edges. While exchanging batteries, care must be taken that main switch 1 is on "OFF". No special precaution is necessary in connecting the M 30 batteries because they are provided with polarized sockets. In connecting the 4F2H battery, the red-marked lead must be connected to the plus terminal of the battery. Should the polarity be reversed, this will become apparent by the galvanometer needle deflecting to the left when switch 3 is turned to position "A".
- f. The battery designations refer to Burgess batteries. Equivalent batteries of any other make can be used.
- g. When connecting or disconnecting a search unit, it is advisable to keep the main switch 1 on "OFF".
- h. If the instrument does not operate properly, one may test the amplifier tube 1H4G and the Amperite ballast tube for continuity between pins 2 and 7. These tubes are accessible by lifting the right-hand panel out of the instrument after the four screws in the corners are removed.
- i. When communicating with the manufacturer about the performance of the instrument, always state the serial number indicated on the name plate.



DETERMINATION OF  $\text{ThO}_2$  IN ORES

## HEXAMINE METHOD.

Transfer a finely ground, accurately weighed sample (about 1 g) of the ore to a 30 ml platinum crucible. Moisten with a little water, add about 20 ml 48% HF, and evaporate to dryness on a steam bath. Repeat the treatment if sample contains much silica. After the HF treatment add about 10 g  $\text{KHF}_2$ , which has been dried in a desiccator, to the crucible and fuse as follows: place the covered crucible over a very low flame and carefully drive off the moisture and reaction gases. Gradually increase the flame until the melt is a clear red hot molten mass over the full flame of a Meker burner. Swirl clear melt to mix fusion. Care must be given throughout the fusion because the material tends to foam, creep, and sputter. Swirl the melt on cooling to form a thin coating on the sides of the crucible. After the crucible is cool place in a large platinum dish and add about 200 ml water and about 25 ml 48% HF. Remove the melt from crucible and break up with a platinum rod. Digest on the steam bath one hour, cool, and filter through No. 42 Whatman. Wash with dilute HF and finally with water. Ignite the residue at  $450-500^\circ\text{C}$  and transfer to a platinum dish with the aid of 15 ml concentrated sulfuric acid and a little cold water. Take the solution to fumes, cool, wash down the sides of the dish with water and take to fumes again. Cool and dilute with about 100 ml water. Digest and stir on the steam bath to dissolve residue

solids. Transfer to a 400 ml beaker. If some insoluble material remains in the platinum dish dissolve this in warm hydrochloric acid (1+1) and add to the beaker. Usually all the material is soluble at this point but if some insoluble remains it will dissolve after the addition of ammonia and sodium nitrite. Nearly neutralize the solution with ammonia and add 10% solution sodium nitrite slowly to effect reduction of  $\text{Ce}^{+4}$  (yellow) to  $\text{Ce}^{+3}$  (colorless). If cerium is present the solution will probably be quite yellow and the addition of sodium nitrite will give a colorless solution unless iron or some other colored ion is present. Make ammoniacal to 10% excess. Allow the solution to cool and the precipitate to settle before filtering through No.40 Whatman paper. Wash with a little cold 2%  $\text{NH}_4\text{Cl}$  - 10%  $\text{NH}_4\text{OH}$  solution. Dissolve the precipitate on the paper with hot hydrochloric acid (1+2), returning the solution to the original beaker. If the precipitate is large it may be necessary to remove the paper from the funnel and slurry with 10-15 hot hydrochloric acid (1+1) in a small beaker. Filter into the beaker containing the dissolved precipitate and wash well with hot hydrochloric acid (1+20)\*. To the combined filtrates and washings add ammonium hydroxide (1+1) until a faint permanent turbidity or precipitate is formed and then add a few drops hydrochloric acid (1+1) to dissolve the precipitate. Dilute to 200 ml and add enough

\* See Note 1



$\text{NH}_4\text{Cl}$  to make a 5% solution of the salt. Add one-half to one ml 10% sodium nitrite and stir well and warm the solution to about 60-70°C. Slowly add 2% hexamine solution (1) until a turbidity is just produced - then add three to four ml more. Stir well and heat (not over 75°C) to coagulate the precipitate and allow the precipitate to settle. Add 1 ml more of hexamine solution to clear supernatant liquid. If no more turbidity is produced (the precipitation is complete) - stir and allow to settle. If more turbidity forms (the precipitation is not complete) add more hexamine in 1 ml portions, allowing the precipitate to settle before each addition until precipitation is complete. After the precipitation has settled filter through No. 40 Whatman paper\*\* and wash with 5%  $\text{NH}_4\text{Cl}$ . Test the filtrate for complete precipitation by adding 1 ml hexamine solution. Dissolve the precipitate on the paper with hot hydrochloric acid (1† 2) finally washing paper with hot 5% hydrochloric acid and repeat hexamine precipitation twice (or until the filtrate from the hexamine precipitation gives no precipitate when made strongly ammoniacal). Dissolve the final hexamine precipitate as before, collecting the solution in a 250 ml beaker. Evaporate to dryness on the steam bath and pour 20-25 ml 10% oxalic acid onto the residue. Stir and then dilute to 100 ml volume. Cover the beaker, gently boil the solution for a few minutes, adjust the volume to 100 ml,

\*\*

See Note 2

and let stand overnight. Filter through No. 42 Whatman, wash with 1-2% oxalic acid, ignite at  $1100^{\circ}\text{C}$ , cool, and weigh as  $\text{ThO}_2$ .

#### NOTES

1. If much  $\text{R}_2\text{O}_3$  other than thorium and rare earth is present it is advisable to either remove the iron by an ether extraction or make an oxalate precipitation at this point. To extract the iron dissolve the ammonia precipitate with hot hydrochloric acid (1+1) and shake with ether (2). The oxalate precipitation is a longer procedure. Evaporate the hydrochloric acid solution of the dissolved ammonia precipitate to dryness and follow the method for oxalate precipitation given above. Ignite the oxalates at  $500^{\circ}\text{C}$  for at least two hours, dissolve in hot concentrated nitric acid, dilute and precipitate with ammonia, dissolve precipitate with hot hydrochloric acid (1+2) and continue with the hexamine separation. If nitric acid will not dissolve the ignited oxalates a pyrosulfate fusion is necessary.
2. It is best to place a pad of macerated filter paper in the apex of the filter paper when filtering all precipitates encountered in this method.

#### References:

1. W. R. Schoeller and A.R. Powell, "The analysis of Minerals and Ores of the Rarer Elements", 2nd Edition, 1940, p. 120
2. W.F. Hillebrand and G.E.F. Lundell, "Applied Inorganic Analysis", p. 106.

## DETERMINATION OF THORIUM OXIDE IN ORES

(1)

## Iodate Method

Transfer a finely ground, accurately weighed sample ( about 1 g) of the ore to a 30 ml platinum crucible. Moisten with a little water, add about 20 ml hydrofluoric acid (48%), and evaporate to dryness on a steam bath. Repeat the treatment if the sample contains much silica. After the hydrofluoric acid treatment add about 8 g potassium acid fluoride, which has been dried in a desiccator, to the crucible and fuse as follows: place the covered crucible over a very low flame and carefully drive off the moisture and reaction gases. Gradually increase the flame until the melt is a clear red hot molten mass over the full flame of a Meker burner. Swirl clear melt to mix fusion. Care must be given throughout the fusion because the material tends to foam, creep, and sputter. Swirl the melt on cooling to form a thin coating on the sides of the crucible. After the crucible is cool, use hot water from a wash bottle to transfer the melt from the crucible to a large platinum dish. Break up the melt with a platinum rod, and then add about 100 ml water, digest on the steam bath 10-15 minutes and then add about 10 ml hydrofluoric acid (48%). Digest on the steam bath 15 minutes, cool, and filter through No. 42 Whatman filter paper and wash with dilute hydrofluoric acid. Transfer the filter paper to a platinum dish, ignite at 450-500°C, cool; add 5 ml nitric acid and 10 ml sulfuric acid and heat cautiously on hot plate to oxidize all carbon. Add more nitric acid when necessary and when the solution is water-white or very light yellow, fume

twice adding a little water each time after cooling the dish in the ice water bath. Transfer the material in the dish to an 800 ml beaker containing 100 ml iced distilled water and stir well. Dilute to 300 ml with water, set on hot plate, add 10 ml conc. nitric acid and 10 ml conc. hydrochloric acid, and boil until solution becomes clear. Usually all the material is soluble at this point but if some insoluble residue remains, it will dissolve after the addition of ammonia and sodium nitrite. Nearly neutralize the solution with ammonia and add sodium nitrite solution (10%) slowly to effect reduction of  $\text{Ce}^{+4}$  (yellow) to  $\text{Ce}^{+3}$  (colorless). If cerium is present the solution will probably be quite yellow and the addition of sodium nitrite will give a colorless solution unless iron or some other colored ion is present. Make ammoniacal to 10% excess. Allow the solution to cool and the precipitate to settle before filtering through a No. 40 Whatman filter paper. Wash with a little cold 2% ammonium nitrate in ammonium hydroxide (1+9). Dissolve the precipitate on the paper with hot nitric acid (1+1) returning the solution to the original beaker. If the precipitate is large it may be necessary to remove the paper from the funnel and slurry with 10-15 ml hot nitric acid (1+1) in a small beaker. Filter into the beaker containing the dissolved precipitate and wash well with hot nitric acid (1+20). Repeat ammonium hydroxide precipitation, washing as above and dissolve this time with 25 ml hot nitric acid (1+1) followed by thorough washing with hot water. Evaporate the filtrate to a 60 ml volume and add 38 ml nitric acid, then cool in ice water bath. Add 3 drops of hydrogen peroxide (30%) and stir, then add 100 ml of a 15% solution of potassium iodate in nitric

acid (1+1). Stir this mixture at times for one hour. Remove from ice water and decant the clear liquid through a #40 Whatman filter paper and transfer the precipitate to the funnel with a 1% solution of potassium iodate in nitric acid (1+9).

After one wash, return the precipitate to the beaker and stir it up with 50 ml of the wash solution. Transfer the precipitate to the filter paper and wash it 3 times with the wash solution.

Dissolve the precipitate with 30 ml of hot nitric acid (1+1). Wash well with hot water. Evaporate the filtrate to 30 ml, cool, the reprecipitate by adding a solution of 4 g potassium iodate dissolved in 30 ml nitric acid (1+1). Stir at frequent intervals, and allow to settle. Collect and wash the precipitate as before, and then dissolve it in dilute hydrochloric acid (1+1) to which a little sulfur dioxide has been added, and wash the filter paper with hot hydrochloric acid (1+2). Add a slight excess of ammonium hydroxide to the filtrate and boil, filter through a #40 Whatman filter paper, and wash with hot 2% ammonium nitrate solution. Dissolve the precipitate in hot hydrochloric acid (1+1), dilute the filtrate to 100 ml and heat the filtrate to boiling. Nearly neutralize with ammonium hydroxide and boil. Then add a hot solution containing 4 g of ammonium oxalate. Add hydrochloric acid (1+1), drop by drop to the solution until a faint turbidity is produced, then add 10 ml of hydrochloric acid (1+1) and allow the solution to stand overnight. The addition of filter pulp will aid in filtering and will give a better product on ignition.

Filter the solution through a #42 Whatman filter paper and wash with a 2% solution of oxalic acid. Transfer to a platinum crucible, ignite at 1000°C until constant weight is obtained.

THE RAPID DETERMINATION OF  $\text{ThO}_2$  IN MONAZITE SAND

Transfer 10.000 gram of the finely ground material to a 100 ml platinum dish. Add 25 ml of sulfuric acid, cover the dish, and heat for one hour at a temperature hot enough to cause fumes of sulfur trioxide to be evolved. Stir occasionally during the heating period. Cool the mixture and pour it onto ice in a 250 ml beaker. Wash the platinum dish with water and stir the resulting solution until the pasty mass is completely in suspension and the ice is melted. Pour the contents of the beaker into a 250 ml volumetric flask, and make up the flask to volume. Mix the solution by shaking; then filter several 50 ml aliquots into dry flasks through 12.5 cm No. 42 Whatman filter papers after discarding the first 20 ml filtered in each case.

Transfer a 50 ml aliquot to a 600 ml beaker and dilute to 450 ml. This should give a pH of between 0.6 and 0.7. Heat the solution to boiling, with constant stirring, and then add slowly still with constant stirring, fifteen ml of a 5% solution of sodium pyrophosphate. Continue the boiling for one or two minutes. Allow the precipitate to settle, then filter the solution through a 11 cm No. 40 Whatman or Schleicher & Schüll No. 589 white label filter paper.

Wash the collected precipitate from the filter paper into the original beaker with a stream of water. Add thirty ml of sodium hydroxide (1 + 1) and about 1 g of sodium peroxide to the slurry, dilute to a volume of 200 ml and boil the mixture for 3 to 4 minutes. Dilute the resulting solution to 400 ml allow the precipitate to settle, then re-filter it through the same filter paper from which it was washed.

Dissolve the precipitate off the filter paper with a little hot hydrochloric acid (1 + 1) and wash with hot HCl (1 + 9) collecting the filtrate in the original beaker. Repeat the sodium hydroxide precipitation and again dissolve the precipitate with hydrochloric acid (1 + 1) as before.

Dilute the filtrate to about 200 ml, and add ammonium hydroxide until a faint cloudiness appears, then add hydrochloric acid dropwise until this cloudiness just disappears. Add two or three ml of an 8% sodium nitrite solution, ten grams of ammonium chloride, and heat the solution to about 60° C. Add dropwise a 2% solution of hexamine until the solution becomes cloudy, then add four ml of the precipitating solution in excess and allow the precipitate to settle, then test for complete precipitation by adding another one ml of the hexamine solution. If the precipitation is complete, heat the solution to about 70° C, allow the precipitate to settle, and then filter the solution through a No. 40 Whatman filter paper. Dissolve the precipitate off the filter paper with hot hydrochloric acid (1 + 1), and wash the filter paper thoroughly with hot hydrochloric acid (1 + 9). Repeat the hexamine precipitation, but this time dissolve the resulting precipitate with hot nitric acid (1 + 2) and wash the filter paper thoroughly with hot nitric acid (1 + 9).

Transfer the solution to a 250 ml beaker, dilute to about 100 ml, and add ten ml of 30% hydrogen peroxide. With the temperature of the solution between 45° C and 50° C, adjust the pH to about 1.5 with dilute ammonium hydroxide. Filter the solution through a No. 40 Whatman, and redissolve the precipitate with hot nitric acid (1 + 2).

collecting the filtrate in 250 ml beaker. Add ten ml of hydrogen peroxide (30%) dilute the solution to 100 ml and determine the amount of titanium dioxide present by comparing with solutions containing known amounts of  $TiP_2$  made under the same conditions either visually in Nessler tubes or with a spectrophotometer measuring the transmittancy of the solutions at 400 millimicrons.

Return the solution to the beaker and again adjust the pH of the solution to 1.5 with ammonium hydroxide as before, and filter the solution through a #40 Whatman filter paper. Transfer the precipitate quantitatively to the filter paper, and wash out the beaker thoroughly with a hot 2% ammonium nitrate solution. Ignite the precipitate in a platinum crucible to  $1000^{\circ}C$  to constant weight. Correct the final weight of the precipitate for the amount of titanium dioxide.

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